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Thermoelectric Energy Conversion Material

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The thermoelectric energy conversion material (thermoelectric material) is the semiconductor with both higher carrier concentration and lower thermal conductivity. The thermocouple consists of p- and n- type thermoelectric materials, and works as a heat<=>electricity energy convertor. The thermocouples are assembled to form a thermomodule. The module requires the advanced joining techniques. In this review, the fundamentals of thermoelectric material and the applications of joining techniques to the thermomodule are summarized, and the higher performance thermoelectric materials with functionally gradient materials(FGM) structures are also introduced.

1. INTRODUCTION

The thermoelectric energy conversion material (thermoelectric material) is the semiconductor with both higher carrier concentration and lower thermal conductivity. The thermocouple consisting of p- and n- type materials is called the thermoelectric conversion element. As is shown in Fig. 1, the element works as Rankine cycle(a) or heat pump(b). This type of thermoelectric energy conversion is carrier transport by heat or electricity. It is one of the solid state energy conversions. Since the element has no mechanical action, the reliable heat <=> electricity energy conversion can be realized without vibration and noise. This conversion is widely applicable in the field from general electronic instruments to aerospace developments. The thermoelectric generators have been applied to free power supplies for space or submarine use. The thermoelectric coolers are now essential to the fabrication process of semiconductors and the precise temperature control of laser units for optical communication.

The thermoelectric elements are commonly used in an assembled form of sheet or cylinder. The assembled elements are called the thermomodule. The cross section of the thermomodule for low temperature use is shown in Fig.2. The thermomodule consists of

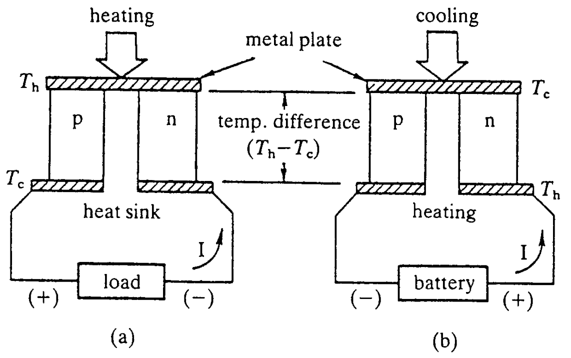

Fig.1

Principle of simple thermoelectric conversion elements of electric generating and cooling. (a) and (b) show the Seebeck and Peltier effects, respectively. I is an electric current.

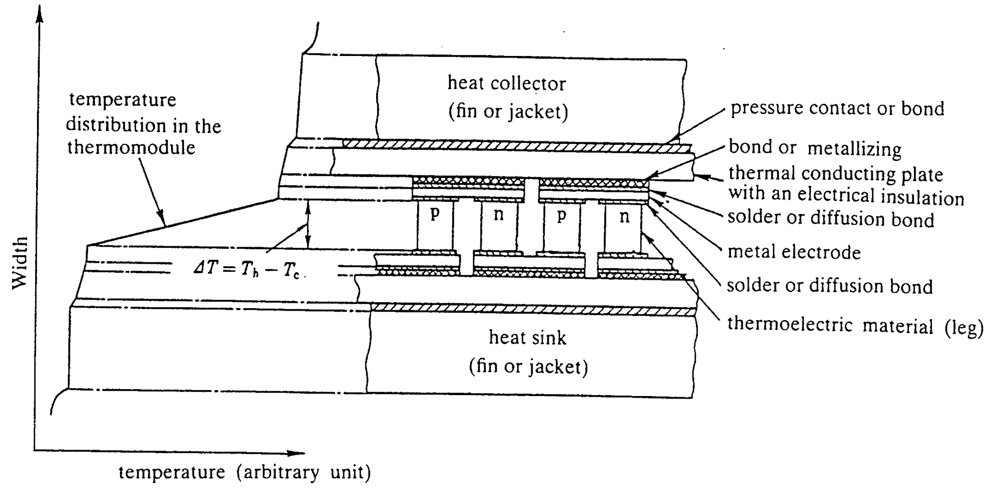

Fig.2 Schematic view of thermomodule and its temperature distribution

many parts such as heat collectors, metal electrodes, thermoelectric materials, heat sinks, etc.. Desired properties for the joints are as follows : i) high mechanical strength, ii) high electrical conductivity with a high thermal insulation, iii) high buffer capacity for semiconducting properties, iv) high thermal conductivity (low thermal conductivity degenerates thermoelectric conversion efficiency), v) high thermodynamical stability (if the components of joining materials diffuse into thermoelectric materials, the deterioration of thermoelectric properties is caused). The comprehensive joining techniques which meet physical, chemical and mechanical demands are essential to the thermomodule.

In this review, the fundamentals of thennoelectric material and the applications of joining techniques to the thermomodule are summarized, and the higher performance thermoelectric materials with functionally gradient materials(FGM) structures are also introduced.

2. FUNDAMENTALS OF THERMOELECTRIC MATERIAL

When T_h and T_c are the hot and cold side temperatures of thermoelectric material, the maximum energy conversion efficiency is given by the following equation:

$$\eta_{\max} = \frac{T_h - T_c}{T_h} \frac{M - 1}{M + T_h / T_c} \tag{1}$$

$$M = \sqrt{1 + \frac{1}{2} Z (T_h + T_c)} \tag{2}$$

$$Z = \frac{\alpha^2}{\rho\kappa} \tag{3}$$

, where α, ρ and κ are the thermoelectric power, the electrical resistivity and the thermal conductivity, respectively [1),2)]. Z is referred to as the figure of merit.

The maximum coefficient of performance for thermoelectric cooling is expressed in the following equation:

$$\phi_{\max} = \frac{T_c}{T_h - T_c} \frac{M - T_h / T_c}{M + 1} \tag{4}$$

When the heat absorber is in adiabatic state, the T_c is lowest. From $\phi_{\max} = 0$, the maximumtemperature difference between T_h and T_c can be obtained 1).

$$\Delta T_{\max} = (T_h - T_c)_{\max} = \frac{1}{2} Z T_c^2 \tag{5}$$

From the (1)～(3) equations, higher conversion efficiency demands higher Z as well as higher T_h. From the (4) and (5), higher Z is essential to thermoelectric cooling or heating. The thermoelectric material has a characteristic Z, and the Z varies with temperature as shown in Fig.3.

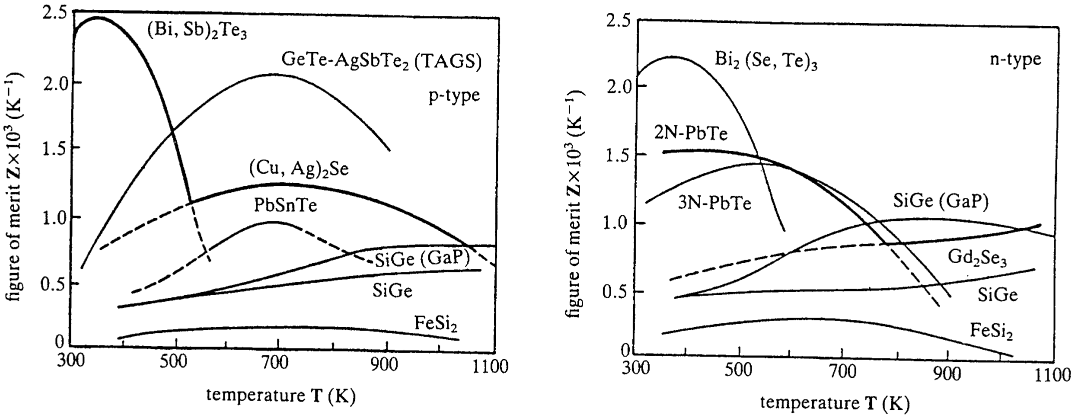

Fig.3 Figure of merits Z as a function of temperature for n- and p-type materials.

3. JOINING TECHNIQUES

3.1 Thermoelectric Material

Figure 4 shows a cross section of the radioisotope fueled thermoelectric generator [3),4)]. It was designed in competition with the generator using SiGe thermomodules. Both the p- and n-type thermoelectric materials(legs) consist of two segments of dissimilar materials, respectively. The p-type segments are $(CuAg)_2Se_3$ and $(Bi,Sb)_2Te_3$. The n-type are Gd_2Se_3 and 2N-PbTe. The Bold Z curves in Fig.3 are given by combination of two segments. The segmented material has a higher Z over a wide temperature range.

The p-type leg is fabricated by sandwiching Fe powder between the $(CuAg)_2Se_3$ and $(Bi,Sb)_2Te_3$ blocks, and subsequent hot pressing the sandwich. The Fe intermediate layer prevents Cu atoms in $(CuAg)_2Se_3$ from migrating to $(Bi,Sb)_2Te_3$.

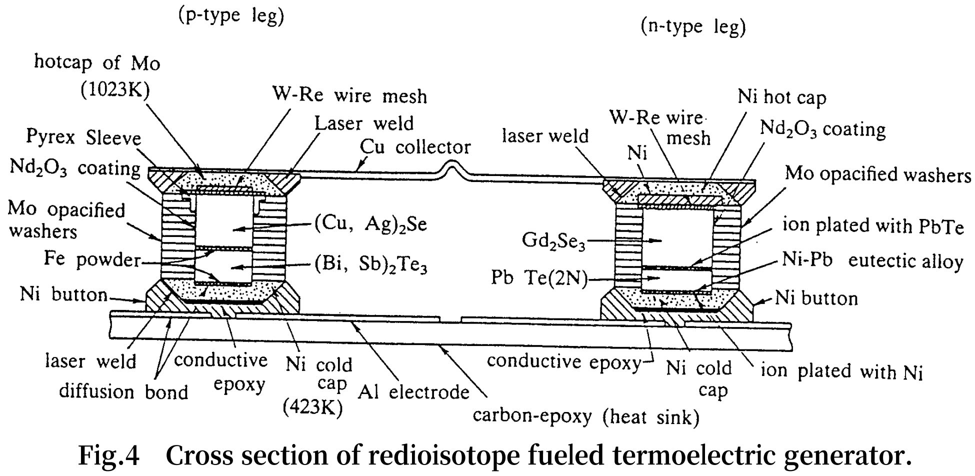

Fig.4 Cross section of redioisotope fueled termoelectric generator. Thermoelectric materials consist of two kinds of segments.

The n-type leg can be also obtained by hot pressing the Gd_2Se_3 and 2N-PbTe blocks. However, direct joining between Gd_2Se_3 and 2N-PbTe degenerates energy conversion efficiency by Thomson effect, because they have a large difference of α at 770K. Undoped PbTe has an effect of decreasing the a difference. By forming the PbTe intermediate layer between Gd_2Se_3 and 2N-PbTe, the heat loss by Thomson effect is successfully reduced. This is the first step to FGM structure .

3.2 Hot and Cold Caps

The bonding l processes of the $(CuAg)_2Se_3$ segment with the Mo hot cap are as follows : i) ion plating a stainless steel plate with Mo, ii) spot welding W-Re meshes to the stainless steel plate, iii) packing (CuAg)2Se3 powders in the spot welded meshes, iv) putting the $(CuAg)_2Se_3$block, the stainless steel plate with the packed meshes and the Mo hot cap in order, v) hot pressing. The Gd_2Se_3 segment is joined to the Ni hot cap by to the same process as the $(CuAg)_2Se_3$ segment. On the other hand, both the $(Bi,Sb)_2Te_3$ and 2N-PbTe segments are joined to the Ni cold caps with Fe powders and Ni-Pb eutectic alloy powders, respectively, by hot pressing. The cap is joined to the Ni button with conductive epoxy. The epoxy relaxes the thermal stresses between the cap and the button, and also acts as a shock absorber at the launching of a rocket. These techniques are almost experiential Advanced joining techiques of forming FGM structures are now promising.

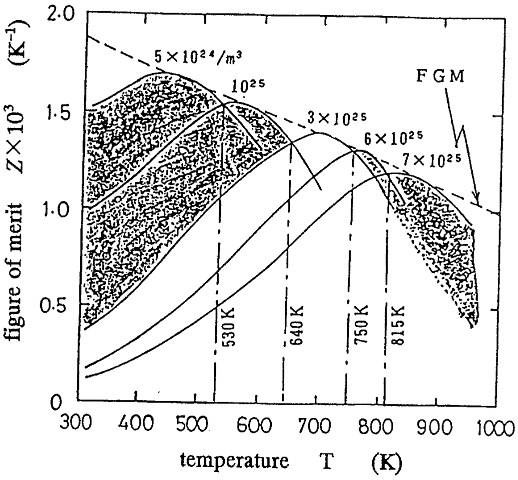

Fig.5

Figure of merits for n-type PbTe with various carrier concentration and the carrier controlled functionally gradient matetials(FGM).

4. THERMOELECTRIC MATERIAL WITH FGM STRUCTURE

Higher Z over a wide temperature range is essential to higlrer η. The variation of Z-T curve of n-type PbTe as a function of carrier concentration is shown in Fig.5. The Z-T curve has a maximum Z-value, and the corresponding temperature is changed with carrier concentration. When the FGM structure is applied to PbTe, the conversion efficiency can be improved remarkably.

Five kinds of PbTe in Fig.5 are joined in sequence so that temperatures of 530, 640, 750 and 815K are distributed at each joined part. This segmented PbTe has a step FGM structure of carrier concentration. It exhibits a larger Z-value by the hatched area than homogeneous PbTe with carrier concentration of $3\times10^{19}/cm^3$. The dotted line in Fig.5 is obtained by changing the camer concentration of PbTe continuously. This graded PbTe has an ideal FGM structure. It exhibits a higher Z over a wide temperature range than the segmented PbTe. It is estimated that the ideal FGM structure improves the average Z by 50% in comparison with homogeneous PbTe, and that the η at Th = 950K reaches 19%.

The maximum temperature available to PbTe is about 950K Refractory SiGe or Gd_2Se_3 is commonly used above 950K. When SiGe or Gd_2Se_3 as well as PbTe has an ideal FGM structure of carrier concentration, and also when SiGe or Gd_2Se_3 is joined to PbTe by FGM techniques of compositional gradient, the maximum temperature is extended to 1400K. The η of homogeneous PbTe is 12%, while the graded material of PbTe/SiGe or PbTe/Gd_2Se_3 is likely to get the $\eta \geqq 27\%$. The FGM structure is effective in improving the energy conversion efficiency.

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