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Study on thermoelectric material and thermoelectric generator

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ABSTRACT

Thermoelectric technology, widely applied to military, aerospace, medicine and microelectronics transforms thermal energy to electricity by the use of thermoelectric materials. In recent years, as the problem of energy and environment looms large, thermoelectric technology is gaining more and more attention. This paper introduces basic principles of thermoelectric technology, summarizes the latest advancement of thermoelectric materials, illustrates the structure of thermoelectric generator and way of heat radiation and discusses current problems of thermoelectric power generation technology as well as methods to improve its generation efficiency.

Key words: Thermoelectric Generation; Thermoelectric Material; Thermoelectric Generator

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INTRODUCTION

The research on thermoelectric technology was dated back to 1940s, and reached its peak in the 1960s when continuous power generation was realized[1]. Office of Space and Defense Power Systems of U.S. Department of Energy commented that thermoelectric power generation "is such a dynamic technology proved to be reliable, durable and capable of working long hours under extreme circumstances." However, constrained by low efficiency and high cost of thermoelectric conversion, thermoelectric technology is less for industrial and civilian use; expect a few application in the front edge such as aerospace and military[2]. In recent years, as the problem of energy and environment looms large and with the development of high-performance thermoelectric materials, thermoelectric technology is gaining more and more attention and becomes a hot issue of research[3].

BASIC PRINCIPLES OF THERMOELECTRICITY

Thermoelectric technology is based on thermoelectric effects, including Seebeck effect, Peltier effect and Thomson effect. It employs thermoelectric materials and transforms thermal energy to electricity.

1. Seebeck effect

As shown in Figure 1, for a circuit constituted of conductor (or semi-conductor) a or b in series, if there are two connectors 1 and 2 at temperature T_h and T_c respectively, there will produce a potential difference between y and z at the open-circuit position of b. Under the same material, the thermoelectricity potential is only related to the temperature difference of two connectors, $\Delta T = T_h - T_c$, and it can be expressed as:

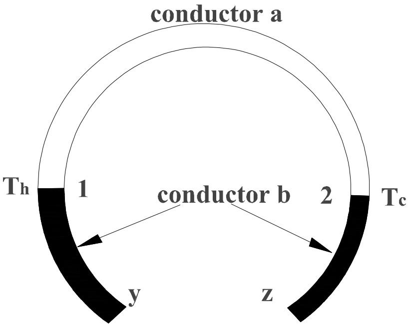

Fig.1Seebeck effect

The Seebeck effect is invertible. When the temperature difference adds or deletes a minus sign, thermoelectricity potential would remain its absolute value with or without a minus sign.

2. Peltier effect

The Peltier effect is the opposite of the Seebeck effect. In Figure 1, if an electromotive force is added at y and z, electric current I is produced in the circuit composed of a and b. At the same time, one connector of the conductors absorbs the heat while the other releases the heat. The experiment found that the heat absorption (release) rate q is in proportion to electric current I, namely:

$$q = \pi_{ab} I \qquad (2)$$

where, π_{ab} is Peltier coefficient, W/A。

3. Thomson effect

When the electric current flows through the conductor which has temperature gradient, besides joule heat, there is also another form of heat to absorb, namely Thomson heat. Experiment has proved that Thomson heat absorbed (or released) per unit time is in proportion to temperature difference ΔT of the conductor and electric current *I*[4]. There is:

$$P = \tau \Delta T I \quad (3)$$

Where, τ is Thomson coefficient, V/K.

These three thermoelectric effects are closely related rather than independent.

Thomson applied the first law and the second law of thermodynamics to three thermoelectric effects and concluded two important formula for coefficients, α , π and τ :

$$\pi_{12} = \alpha_{12} T \qquad (4)$$

$$\tau_1 - \tau_2 = T \frac{d\alpha_{12}}{dT} \qquad (5)$$

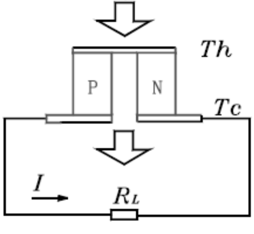

Fig.2 Thermoelectricity leg

4. Basic principles of thermoelectric generator

A p-type thermoelectricity component and ann-type thermoelectricity component were connected with metallic electrodes at the hot-end, which is called thermoelectricity couple or temperature difference uncouple. As is shown in Figure 2, the open-end of the thermoelectricity couple is connected with an external load whose resistance is r_L. When the electric current moves through the circuit, the electric power of the load is $I^2 r_L$. Consequently, a generator that converts thermal energy to electricity is obtained [5].

THERMOELECTRIC MATERIAL

1. Selecting standard for thermoelectric materials

In order to increase the efficiency of the thermoelectric generator, it is necessary to increase the optimum value Z of thermoelectricity leg.

$$Z = \frac{\alpha^2{}_{pn}}{\left(\sqrt{k_p \rho_p} + \sqrt{k_n \rho_n}\right)^2} \qquad (6)$$

Optimum value Z is the standard of evaluating the quality of a certain materialin the research of thermoelectric materials.

$$Z = \frac{\alpha^2}{\rho \kappa} = \frac{\alpha^2 \sigma}{k} \qquad (7)$$

In real practice, the dimensionless optimum value Z of electric material with single temperature difference is expressed by its multiplying with absolute temperature.

$$ZT = \frac{\alpha^2 T}{\rho \kappa} = \frac{\alpha^2 \sigma}{k} T \qquad (8)$$

From the equation, it is known that to find materials with high optimum value, the only method is to enhance the Seebeck coefficient and electrical conductivity and reduce thermal conductivity of the material.

2. Major thermoelectric materials

At the present, common thermoelectric materials are bismuth telluride (Bi_2Te_3) and its alloys, plumbous telluride (PbTe) and its alloys and silicon germanium (SiGe) alloys.

2.1 $Bi_2Te_3$and its alloys

Te’s atomic number is 52 and Bi’s atomic number is 83. Among all stable compound of element Bi and Te, Bi_2Te_3has the largest molecular weight. Bi_2Te_3’s melting point is 585° C, and its density is 7.86g/cm^3 .The structure of Bi_2Te_3 is shown in Figure 3. The stoichiometry of $Bi_2Te_3$is beyond control during the growth of the crystal. For compound semiconductors, chemical ratio has a significant influence on crystal property. If Bi is excessive in the crystal, a p-type material will be obtained. If Te is excessive, an n-type material will be obtained [6].

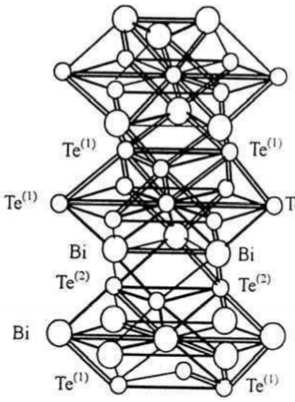

Fig.3Crystal structure ofbismuth telluride

Thermoelectric properties of melt $Bi_2Te_3$and its alloys are distinct between parallel and vertical to the cleavage plane. At 300K, Bi_2Te_3thermoelectric unicouple reaches the largest optimum value. The electrical resistivity of p-type and n-type materials is $1.0\times10^{-5}\,\Omega \bullet m$. Their Seebeck coefficients are $185\,\mu V/K$ and $-205\,\mu V/K$ respectively. k is about $1.9\,W/(m \bullet K)$. The optimum value of thermoelectric unicouple is $2.0\times10^{-3}K^{-1}$.

Metals like copper, silver and gold diffuse fast under heat in Bi_2Te_3 crystal, even if under low temperature. Figure 4

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shows the diffusion coefficient of copper in bismuth telluride. Bi_2Te_3has two pseudobinary systems, namely Bi_2Te_3-$Bi_2Se_3$and Bi_2Te_3-Sb_2Te_3. The composition of each may change within a range. The best p-type thermoelectric material is close to $Bi_{2-x}Sb_xTe_3$and x≈1.5. The best n-type thermoelectric material is close to $Bi_2Te_{3-y}Se_y$ and y≈0.3. Figure 5 shows the optimum value of alloy and Bi_2Te_3 of pseudobinary system[7].

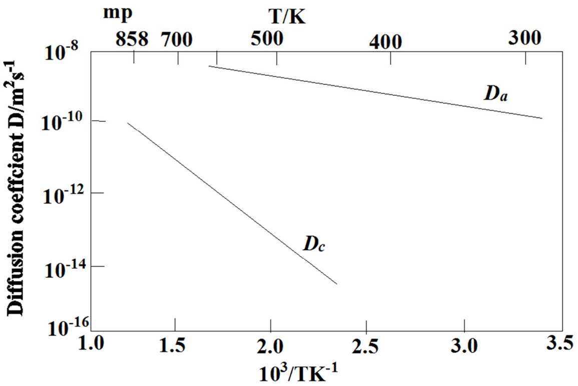

Fig.4 Diffusion coefficient of copper in bismuth telluride

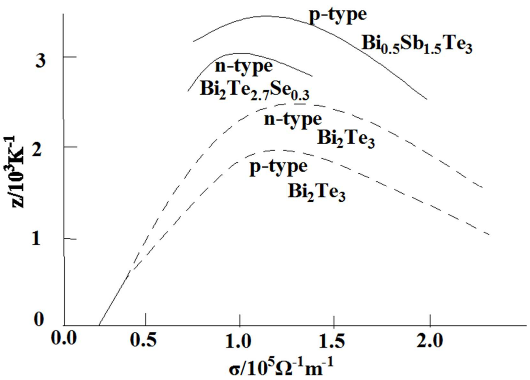

Fig.5 The optimum value of alloy and Bi_2Te_3 of pseudobinary system

2.2 PbTe and its alloys

Plumbous tellurid is an intermetallic compound with a cubic crystal structure. The melting point of plumbous telluride is 922°C. The band-gap ratio is 0.30 eV, twice as that of bismuth telluride. It is used for thermoelectric power generation between temperatures 300-900K. Figure 6and Figure7 show the variation of electrical resistivity, the Seebeck coefficient, the thermal conductivity and the optimum value of PbTe under different mixture versus temperature[8].

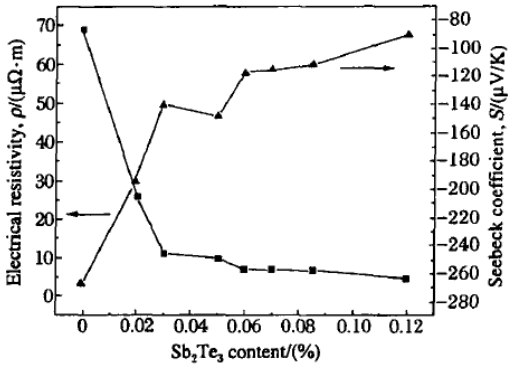

Fig. 6 Relationship among the electrical resistivity, Seebeck coefficient and Sb_2Te_3 content for PbTe

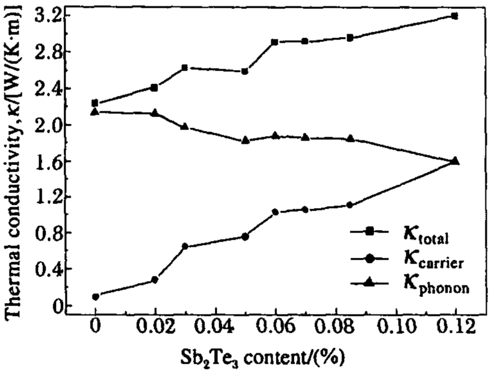

Fig. 7 Dependence of the thermal conductivity on Sb_2Te_3 content for PbTe

Table 1shows the performances pf PbTe and its alloys and other moderate-temperature materials

Table. 1 performances pf PbTe and its alloys and other moderate-temperature materials

Material	Type	Dopant	K $(W/(m \bullet K))$	$Z_{max}(10^{-3}/K)$
PbTe	N	Br+Pb	2.0	20
PbTe	P	Ag,K,Na	2.0	1.7
PbTe75%+SnTe25%	N	PbC12+Pb	1.2	1.35
GeTe10%+$AgSbTe_2$90%	P		1.5	1.4-1.5

2.3SiGe alloys

The solid solution formed by Si and Ge according to a certain proportion becomes the best high-temperature thermoelectric material as the thermal conductivity of crystal is lowered greatly. Currently, common solid solutions are $Si_{0.70}Ge_{0.30}$,$Si_{0.80}Ge_{0.20}$and $Si_{0.85}Ge_{0.15}$.Figure 8 shows the optimum values of SiGe alloy versus temperature [9], [10].

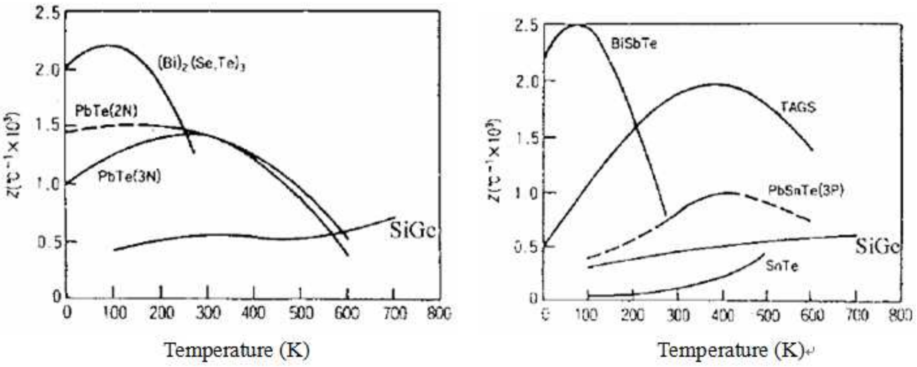

Fig.8 Optimum values of thermoelectric materials

THERMOELECTRIC GENERATOR

1. Thermal source

Classified by thermal sources, thermoelectric generators include radioisotope thermoelectric generator, nuclear reactor thermoelectric generator, alkylate fuel thermoelectric generator and low-level heat thermoelectric generator, etc.

Classified by operating temperatures, thermoelectric generators include high-temperature thermoelectric generator, moderate-temperature thermoelectric generator and low-temperature thermoelectric generator. High-temperature thermoelectric generator works at 700° C or above with silicon germanium alloys (SiGe) as the most common material. Moderate-temperature thermoelectric generator works at 400° C-500° Cwith plumbous telluride(PbTe) as the most common material. Low-temperature thermoelectric generator works at below 400° C with bismuth telluride(Bi_2Te_3) as the most common material.

2.Transducer

Thermoelectric transducer is the core of thermoelectric generator. There are three types of design calculation of thermoelectric transducer:

1) With power and load voltage to be given quantity, design a thermoelectric transducer working under the highest efficiency.
2) With power of thermal source, thermoelectric materials and the highest temperature to be given quantity, design a thermoelectric transducer of the maximum power working under certain load voltage.
3) According to the working temperature at the hot-end and the cold-end, figure out the parameters of the thermoelectric transducer.

3.Radiator

Thermoelectric generator only converts a small percentage of energy provided by the thermal source to electricity while the rest, nearly 85%, is diffused through the cooling system. The cooling system works in different ways according to performance parameters or working conditions of thermoelectric generator. Its design is very complex.

3.1 Rib-shapedradiating fin

The calculation about rib-shaped radiating fin is very complicated, with the following principles to follow:
1) The radiating fin should be good at thermal conductivity. The thinner, the better.
2) The radiating fin and the shell should be manufactured at one time. If made separately, the two parts may not connect well, resulting in poor conductivity. When manufacturing these two parts, attention should be paid to tightness.
3) The radiating fin and the shell should be made from the same material. Otherwise, due to distinct thermal expansion coefficients, the radiating fin may get loose and fall off from the generator, which would influence the thermal conductivity.
4) If manufacturing permitting, try to reduce the distance between radiating fins while increasing the number of radiating fins in order to acquire higher rib effect coefficient.
5) The displacement of radiating fin should not prevent it from contacting the moving fluid.
6) The size of radiating fin is decided by rib effect coefficient and structural strength. Attention should also be paid to power-weight ratio of the generator, power volume ratio, convenience and other relevant factors. We shouldn’t only consider diffusion effect while neglecting other factors.

3.2 Radiating coating

In real practice, the shell of thermoelectric generator is covered by a selective coating which is designed for diffusing the waste heat of thermoelectric generator, resisting heat absorbed from the environment through radiation or convection, thus keeping the generator at a cooling temperature. In addition, the coating can also protect the generator from oxidation or corrosion.

3.3 Heat Pipe radiation

Heat pipe can transport the heat from one place to another. Owing to its fast thermal conductivity, there is almost no heat loss, winning it the name of “superconductor of heat”. Heat pipe is applied to spaceradioisotope thermoelectric generator (RTG). If it is installed on the RTG’s shell rib, the temperature at the cold-end can be lowered. If installed on RTG’s heat collector, it can better collect the radiated heat and convert it to the heat controlling system. The high-power thermoelectric generator (eg: type 8550) manufactured by the Global Company is installed with heat pipe radiator. Figure 9 shows the structure and working principle of heat pipe radiator [11], [12].

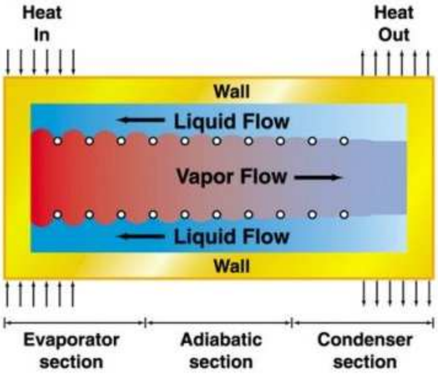

Fig.9 Structure and principles of heat pipe

3.4 Phase change for energy storage

PCM (Phase Change Material) refers to the material whose form changes with the temperature and can provide potential heat. The process in which PCM transforms from liquid state to solid state is called phase change process.

During the process, a large amount of potential heat will be absorbed or released. Many organic materials experience solid-solid phase change below the melting point. This phase has many advantages, such as little change in volume, possessing high melting point and no need for supercoiling, etc.

Tongji University developed a composite material with energy stored in nano-graphite. The conductivity coefficient of nano-graphite PCMs is 10 times even 100 times that of existing PCMs. The phase change temperature changes continuously between -40--70°C and the energy density can reach 150-250J/g. After 1000 times of recycling, only 5% suffers performance deterioration.

CONCLUSION

In modern era when green energy and renewable energy become the dominant source of energy, thermoelectric technology will be more and more applied to many fields. The promotion of thermoelectric technology is largely depended on the research and development of more optimum thermoelectric materials. Materials of low dimensional, gradient change or integrated with several elements will improve the optimum value of thermoelectric materials, which leads the current research.

The temperature-electricity technology can achieve good effect of energy-saving with relatively low cost. Recently, there are many new concepts and practices springing up in the thermoelectricity field, including the high energy density thermoelectric power generation module, the cogeneration system and the heating cycle thermal combustion system. With the research on thermoelectric materials going deep and the manufacturing technology becoming mature, thermal performance and thermoelectric technology will be more advanced. Industrial waste and waste heat from waste incineration will be employed and served for more use. We believe thermoelectric technology will bring great changes and innovation to our life.

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