A Study on the Preparation Method of Thermoelectric Power Generation Module

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Abstract. The thermoelectric power generation module is a device that directly converts thermal energy into electrical energy. It has many advantages such as noise-free, pollution-free, high reliability, long service life and so on. The traditional thermoelectric power generation module has such disadvantages as complicated preparation process, processing pollution, great material wastage, etc. A method for preparing the thermoelectric power generation module has been studied in this article. Firstly, a silver electrode is made on a ceramic substrate, and then the template is placed on the electrode and stacked layer-by-layer with thermoelectric materials following the lamination technique; subsequently it is sintered into a galvanic couple arm and then the thermoelectric power generation module is made after encapsulation. The preparation method is able to effectively avoid the wastage of thermoelectric materials and processing pollution, and is especially suitable for the wide temperature range operation mode. It is also able to exert the best performance of each material segment and effectively improve the working efficiency of the power generation module.

1. Introduction
The thermoelectric power generation module is a fully static power generation method that uses thermoelectric materials to directly convert thermal energy into electrical energy. It has many advantages such as compact structure, no noise, no wear, no leakage, flexible mobility, and reliable performance. [1-5] At present, as for the thermoelectric generation module, the preparation method generally adopts the zone melting technique or the powder metallurgy method to obtain the thermoelectric bulk material, which is sliced and electroplated the solder layer, and then subjected to the cutting lines to obtain a desired size thermocouple arm. After that, the thermocouple arm is placed on the copper electrode sheet of the ceramic substrate one by one and finally sintered at a high temperature to achieve the series connection of the P type and N type thermoelectric materials and encapsulation to obtain a thermoelectric power generation module. [6]

However, many experimental studies have shown that the preparation technology of the existing thermoelectric power generation modules is complex and inefficient. In addition, there is a great deal of loss and pollution in the cutting process of the thermoelectric bulk material, and there is a phenomenon that the electrode and the welding material have a high degree of exfoliation during the operation, so the defective rate of the product is high. In addition, a common feature of homogeneous thermoelectric materials is that their best performance (the thermoelectric Figure of merit, ZT value) only occurs at a certain temperature or temperature zone. For example, the ZT value of the Bi₂Te₃ system is about 1 at about 400K, but it drops to 0.75 at 300K and 500K. If the thermoelectric power generation module operates in a wide range of temperature difference, for example, the temperature
difference between the hot end of the spacecraft operating in deep space and the outer layer is more than 1000°C, any homogenous thermoelectric material obtained according to the current preparation method of the thermoelectric power generation module cannot play its best performance. [7]

In view of the deficiencies of the above thermoelectric generation module manufacturing technology, this paper studies a method for preparing a thermoelectric power generation module. The method firstly prepares a silver electrode and a mask plate. Then, the thermoelectric material is layer-by-layer coated on the silver electrode ceramic substrate based on its used temperature gradient by using a mask plate. At last, the galvanic arm was once formed by sintering. This preparation method avoids thermoelectric material loss and processing pollution and is particularly suitable for a wide temperature range operation mode, which can exert the best performance of each material segment, and the preparation method is simple and feasible, and has a good application value.

2. Preparation scheme

The preparation process of the thermoelectric power generation module in this paper includes the following steps: preparation of silver electrodes and mask plates, coating of thermoelectric powder materials, sintering of thermoelectric substrates, insulation, and encapsulation and solidification, as shown in Fig. 1.

![](image)

Fig.1 Preparation process of thermoelectric power generation module

2.1. Preparation of silver electrodes and mask plates

Firstly, a screen printing plate is designed according to the assembly form of the thermoelectric power generation module, and then the screen printing plate is printed on the surface of a ceramic substrate through a sintering process to obtain a first silver electrode, and the surface screen structure thereof is shown in Fig. 2. At the same time, a second silver electrode is fabricated on the surface of another ceramic substrate with the same shape and size by the same process, and its surface structure is shown in Fig. 3. Among them, in order to ensure excellent performance of the silver electrode, the selected ceramic material is an alumina substrate because the alumina material has excellent high thermal conductivity.[8] The sintering process has a sintering temperature of 850 to 950°C and a sintering time of 30 to 60 minutes.
After the first silver electrode and the second silver electrode are obtained, the solder paste (thickness from 30 to 50 um) is printed using the designed screen printing plate and used as the buffer connection layer of the first silver electrode and the second silver electrode.

Then, the first mask plates (1 in Fig. 4) and the second mask plates (3 in Fig. 5) each having the same shape and size as those of the ceramic substrate were fabricated, and the same m blocks.
Fig. 5 Schematic diagram of the second mask structure

Among them, the first mask plate is provided with a first receiving groove (2 in Fig. 4) distributed according to the silver electrode pattern, and the second mask plate is provided with a second receiving groove distributed according to the pattern of the silver electrode (4 in Fig. 5). The first receiving tank is for coating the thermoelectric powder material and serves as a battery P-type electric coupler arm. The second receiving tank is used for coating the thermoelectric powder material and serves as a battery N-type electric coupler arm. The first mask plate and the second mask plate are transparent.

2.2. Coating thermoelectric powder materials

After obtaining the first silver electrode, the second silver electrode, the first mask plate, and the second mask plate, application of the thermoelectric powder material to the P and N type regions is started to obtain first and second thermoelectric substrates. Its preparation method is as follows:

1) Preparation of the First Thermoelectric Substrate
   (1) P1, P2, P3, … Pm layer thermoelectric powder materials are respectively produced, which are obtained by using a mixed ball mill, adding a binder and a dispersant grinding method;
   (2) aligning the first mask of the first block with the first silver electrode and overlaying the P1 layer of thermoelectric powder material into the first receiving tank of the mask, and compacting;
   (3) align the first mask of the second block with the first mask of step (2), and apply the P2 thermoelectric powder material to the first receiving tank and compact it;
   (4) Circulate in the manner as described in step (3) until the first mask of the m block is aligned with the first mask of the (m-1) block and the Pm layer of the thermoelectric powder material is coated. All the first masks are then removed, resulting in a first thermoelectric substrate. The foregoing P1, P2, P3, … Pm layer thermoelectric powder material temperature relationship: P1 > P2 > P3 … > Pm;

2) Preparation of Second Thermoelectric Substrates
   (1) Separate N1, N2, N3…Nm thermoelectric powder materials;
   (2) aligning and overlaying the second mask of the first block with the second silver electrode, and coating the N1 thermoelectric powder material into the second receiving tank of the mask, and compacting;
   (3) aligning the second mask of the second block with the second mask of step (2), and coating the N2 thermoelectric powder material into the second receiving tank and compacting;
   (4) Circulate in the manner described in step (7) until the second mask of the m block is superimposed on the second mask plate of the (m-1) block and coated with the Nm layer of thermoelectric powder material. All the second masks were removed to give a second thermoelectric substrate. The temperature relationship of the Nm, N2, N3,…Nm layer thermoelectric powder materials is: N1 < N2 < N3 … < Nm.
Through the above steps, the first thermoelectric substrate and the second thermoelectric substrate can be obtained. Among them, the first layer of P and N on the first silver electrode has the best thermoelectric optimum temperature, and then it gradually decreases toward the second silver electrode, that is, the first layer P and N on the second silver electrode have the best thermoelectric power. Suitable for the lowest temperature.

The state in which the first and second masks of the first silver electrode are stacked is shown in Fig. 6, and the state in which the first and second masks of the second silver electrode are stacked is shown in Fig. 7.

![Fig. 6 Superimposition of the first and second masks on the first silver electrode](image1)

![Fig. 7 Overlay of the first and second masks on the second silver electrode](image2)

2.3. Thermoelectric substrate sintering
The first thermoelectric substrate and the second thermoelectric substrate are aligned and superimposed, and then placed in a high-temperature atmosphere furnace and sintered in an inert atmosphere at a sintering temperature of 450 to 650° C. to obtain respective thermocouples of the P-type electrode and the N-type electrode respectively. Arm and solder connection layer.

2.4. Insulation and encapsulation curing
After obtaining the thermocouple arm and solder connection layer, the final step is to draw the red and black wires. Red and black wires are drawn on the P-type and N-type electrodes, respectively, and coated with insulating and insulating adhesive, and then the package is cured.

According to the above four preparation steps, a laminated thermoelectric power generation module can be prepared.

3. Application of preparation method
A thermoelectric power generation module is now being prepared using relevant procedures to demonstrate the feasibility of related technologies. The first is to make a silver electrode and a mask
plate, in which the first mask plate and the second mask plate are three pieces. The BiTe-based material is used as a low-temperature layer for each of the P-type and N-type electrodes, the PbTe-based material is used for each of the P-type and N-type electrodes, and the SiGe-based material is used as a high-temperature layer for each of the P-type and N-type electrodes.

3.1. Preparation of the First Thermoelectric Substrate

The P-type SiGe thermoelectric powder material (i.e., P₁ thermoelectric powder material) is prepared under the condition of a temperature of 800K; a P-type PbTe thermoelectric powder material (i.e., P₂ thermoelectric powder material) is produced at a temperature of 600K. Finally, under the condition of 400 K, P-type BiTe thermoelectric powder material (i.e. P₃ thermoelectric powder material) was produced. Each of the foregoing thermoelectric powder materials is applied to the receiving groove of the corresponding layer by using three first mask plates. Finally, the three first mask plates are removed to obtain the first thermoelectric substrate.

3.2. Preparation of the second thermoelectric substrate

At a temperature of 400 K, an N-type BiTe thermoelectric powder material (i.e., a N₁ thermoelectric powder material) is produced; at a temperature of 600 K, an N-type PbTe thermoelectric powder material (i.e., N₂ thermoelectric powder material) is produced. N-type SiGe thermoelectric powder material (i.e., N₃ thermoelectric powder material) was produced at a temperature of 800 K. Each of the foregoing thermoelectric powder materials is applied to the receiving groove of the corresponding layer by using three second mask plates, and the three second mask plates are finally removed to obtain the second thermoelectric substrate.

3.3. Thermoelectric substrate assembly

The first and second thermoelectric substrates prepared as described above are sintered, insulated, and packaged and cured to obtain a laminated thermoelectric power generation module.

The relevant indexes and performances of the thermoelectric power generation module prepared by using the preparation method of this article and the conventional preparation method are shown in Table 1, respectively.

| Preparation method | Processing time / each | Preparation costs / each | Power generation efficiency |
|--------------------|------------------------|-------------------------|----------------------------|
| Coating method     | 4 h                    | 30 RMB                  | 15%                        |
| Traditional method | 8 h                    | 40 RMB                  | 12%                        |

After comparison, the time for producing the thermoelectric power generation module using the stacking technology of this paper is shorter than that of the conventional method for preparing the thermoelectric power generation module, the cost is reduced, the technology is obviously improved, and the thermoelectric performance of the battery is higher. The method for preparing a thermoelectric power generation module has the following beneficial effects:

1) P and N-type thermoelectric substrates are obtained by using a thermoelectric material powder layer-by-layer coating method, and the P-type thermoelectric and N-type thermoelectric temperatures are increasing in the opposite direction, so that it is not necessary to perform P and N as in the prior art. Pre-preparation of thermoelectric bulk materials. The coating method can solve the contradiction between the reduction of the thermal conductivity and the improvement of the material properties of the block materials, the reduction of wire cutting of the galvanic welding arm, the tin plating, and the preparation of the thermoelectric film target material, thereby the preparation process is simpler and avoids. The poor welding of the product and the non-uniformity in the cutting process result in low
material loss and no pollution. Significantly increase the preparation efficiency and reduce the preparation cost, so as to truly achieve the relative balance between technology and cost.

2) The thermoelectric powder material is filled into the receiving groove of the mask plate by means of coating, so that all the receiving grooves can be completely filled at one time; on the other hand, the particle size of the powder is inhomogeneous, and thus compared with the traditional as for the printing method, the coating method not only does not require any particle size, but also easily achieves a large thickness of filling. According to the analysis of the ZT optimal value, the power generation efficiency of the battery increases with the increase of the thickness of the material. Therefore, filling the thermoelectric powder material with the coating method can fully exert the performance of the material.

3) In the process of preparing the P and N electrodes of the battery, thermoelectric materials with different optimal operating temperatures may be selected according to the direction of the temperature gradient (for example, PbTe and BiTe series thermoelectric powder materials may be used) so as to make the materials work near the temperature with the largest ZT value respectively. Combining with the coating thickness of the thermoelectric material, the thermoelectric power generation efficiency of the finally obtained laminated thermoelectric power generation module can be further effectively and greatly improved.

4) In the preparation process of this paper, the thermoelectric material is first grinded and crushed and then sintered, and grain boundaries containing many micrometers or even nanostructures can be well obtained, which can effectively reduce the thermal conductivity of the phonons, thereby making the thermoelectricity of the materials superior. The value is greatly improved.

4. Summary

This paper proposes a new method for the preparation of thermoelectric power generation module. The method adopts the laminating principle, and the P and N thermocouple arms are prepared by coating the thermoelectric material layer by layer on the alumina ceramic substrate through a mask plate and sinter forming. Two kinds of thermocouple arms are assembled and sintered and packaged to obtain a thermoelectric power generation module. This method has many advantages compared with the conventional thermoelectric generation module preparation process. First, the method reduces many processes, can effectively shorten the preparation time, and significantly increase preparation efficiency. Second, it realizes low material loss and pollution-free preparation, and the preparation cost is obvious. Lower; third is the use of coating method filling layer by layer can give full play to the best thermoelectricity value of each thermoelectric powder material, improve the temperature difference power generation module thermoelectric power generation efficiency. The preparation method of this paper is simple and feasible. It can give full play to the best performance of each material segment. It is especially suitable for wide temperature range work mode and has good application value.

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