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Interface evolution analysis of graded thermoelectric materials joined by low temperature sintering of nano-silver paste

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ABSTRACT

Lead free solder $Sn_{96.5}Ag_{3.0}Cu_{0.5}$ (SAC305) and nano-silver paste were used to connect graded thermoelectric (TE) arms, respectively. A series of harsh aging tests were carried out on joints of both p-type and n-type graded TE arms. The results showed that nano-silver paste printed by low-temperature joining technique was much more suitable for the stable connection of TE materials working in medium temperature range. 316 stainless steel and nickel were proved effectively as diffusion barrier layers in p-type junctions. While for n-type TE junctions, when aging at 300 °C, (Fe, Cr, Te) ternary alloy could be detected at $Bi_2Te_{2.7}Se_{0.3}$/316 stainless steel interface. The formation of ternary compound realized fine metallurgical interconnection which was benefit for the improvement of joint strength. The average joint strength for p-type and n-type junctions in graded TE arms were above 20 MPa and 30 MPa, respectively.

1. Introduction

Thermoelectric generators (TEGs) which can realize direct conversion between thermal energy and electricity have been extensively researched recently in the field of waste heat recovery, due to their features such as environment protection, reliability and small size and weight [1–4]. To maximum the conversion efficiency, the theory of functionally gradient material (FGM) was firstly proposed by Ioffe [5] in 1960. Based on this theory, TEGs can be applied at a temperature range of several hundreds of degrees [6]. One type of FGM is composed by single material with continuous carrier concentration [7–9]. This kind of design avoids common problems existing in the connection of dissimilar materials. However, the consequent degradation of property caused by carrier diffusion is unavoidable. Another type is segmented or graded-based FGM which is more practical nowadays [10–12]. In this way, research mainly focuses on the connection of dissimilar materials. The mismatch of coefficient of thermal expansion (CTE), diffusion and reaction among materials at the interfaces during long and harsh working conditions may lead to deformation and cracks at the joints, which further threat to the stability and properties of the TEGs.

Generally speaking, the choice of joining techniques among three dimensional TE materials and electrodes depends on the working temperature range of TEGs. Till now, much work has been carried out on the connection of various TE material and electrodes. Besides the application of processes such as sputtering, electroplating and chemical vapor deposition of electrode on the properly prepared TE leg, bonding methods with various of lead free solders like Sn–Ag and Sn–Ag–Cu alloys are usually applied for TEGs working in low temperature range (< 200). In our previous work, SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couple was fabricated at 260 °C. SnTe–SbSn compounds could be found at the interface which indicated a formation of metallurgical interconnection [13]. Many similar studies have also been done on the interfacial reactions in Sn/BixTey and so on [14,15]. C. Zanden et al. [16] proposed a new type of solder matrix nano polymer composite (SMNPC) formed by liquid-phase infiltration of a Sn–Ag–Cu matrix into a fiber mesh. Investigations of mechanical and thermal properties of the SMNPC showed that it can be a useful composite for thermal management applications compared with traditional solders. However, limited by the low melting point of Sn based solder (< 300 °C), there need

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ways to realize stable connections among TE materials working at medium or high temperature range.

For medium- and high-temperature applications, the connections among TE materials and electrodes are often realized by hot pressing (HP) or spark plasma sintering process (SPS). X.C. Fan et al. [17] took Mo–Cu and Mo–Ti alloys as buffer and barrier layers and achieved connections between Ni electrodes and $Yb_{0.3}CoSb_{12}$ by SPS. The aging tests at 550 °C proved that the joints had high thermal duration stability. H.Y. Xia et al. [18] bonded Nb foil directly to PbTe-based material by HP at 700 °C. Intermetallic compounds were detected at the interfaces in the following tests. Ti–Al/$Yb_{0.6}Co_4Sb_{12}$ TE joints were fabricated by M. Gu et al. by SPS [19]. The investigation also proved that nice stability and shear strength of the junctions could be obtained by adjusting the content of Al in Ti–Al alloys. All above showed that both HP and SPS process could realize fine connections between TE material and electrode, while harsh parameters required during the process such as high temperature and certain pressure which easily led to the formation of defects would definitely imped the development of these methods.

Recently, a new joining technique called solid–liquid interdiffusion bonding (SLID) was proposed. W. P. Lin et al. [20] realized the connection between bismuth telluride chips and alumina electrode by SLID with Ag–In system. The study showed that Ag_xIn_y compounds formed at the interface and the joint had a high melting point. T.H. Chuang et al. [21] enhanced the bonding strength of (Pb, Sn)/Cu joints by SLID method as well. However, the high cost and the use of toxicity indium in this method would threat to the property of TEGs and limit the wide application of Ag–In system by SLID.

In this paper, low-temperature joining technique (LTJT) by silver sintering was applied to achieve fine connection in graded TE material system. This technique has been widely spread in the manufacture of power electronic devices [22,23] while similar work in TEGs is still limited. M. Edwards et al. [24] sintered SiGe leg to Cu metallized AlN substrates by nanosilver paste at 310 °C. The joints proved fine strength and stiffness at room temperature. However, the sintering temperature set in their work was relatively higher which might do harm to the properties of the modules and limit the extensive application. In our study, to fabricate graded TEGs working between room temperature and medium temperature (< 400 °C), $Bi_{0.5}Sb_{1.5}Te_3$ and $AgSbTe_{2.01}$ were chosen for p-type TE arm while $Bi_2Te_{2.7}Se_{0.3}$ and $Ag_{0.8}Pb_{22.5}SbTe_{20}$ for n-type arm, respectively. Nanosilver paste was applied as the solder to realize fine connection among different TE materials. Ni and 316 stainless steel were taken as diffusion barrier layers, respectively. The interfacial evolution behavior of graded TE joints would be investigated during harsh aging treatments.

2. Experimental details

TE materials in this paper such as p-type $Bi_{0.5}Sb_{1.5}Te_3$ applied in low temperature range, p-type $AgSbTe_{2.01}$ and n-type $Ag_{0.8}Pb_{22.5}SbTe_{20}$ (LAST) used in medium temperature were fabricated by mechanical alloying (MA) and following spark plasma sintering (SPS) process. Pure material was weighed out in corresponding stoichiometric ratio in an argon-filled glove box, charged into a stainless steel vial and milled for certain time. The alloyed powders were then put into graphite dies and pressed to obtain bulk samples. For n-type $Bi_2Te_{2.7}Se_{0.3}$, which was suitable for low temperature, was obtained from a commercial supplier.

Nickel with a thickness of about 2 μm was sputtered on the surface of p-type $Bi_{0.5}Sb_{1.5}Te_3$ as a diffusion barrier layer by magnetron sputtering process while 316 stainless steel was chosen for other TE materials. Before connecting, silver was sputtered on the surface of all samples to enhance joint strength. Promising lead free solder alloy $Sn_{96}.5Ag_{3.0}Cu_{0.5}$ (SAC305) and nano-silver paste supplied by Prof. Quo-Quan Lu were applied in turn. Layered structures of n-type and p-type TE couples were shown in Fig. 1.

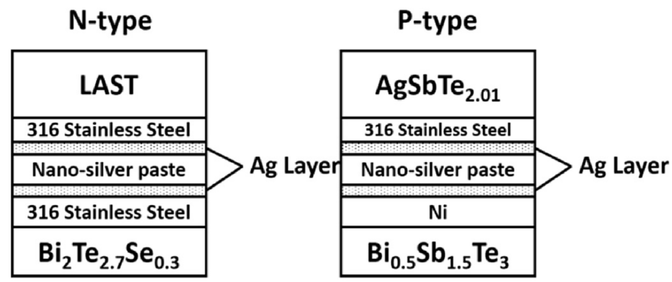

Fig. 1. Schematic presentation of p-type and n-type couples with layered structure.

The sintered joints were kept in a furnace in air environment and suffered a series of aging treatments. After aging tests, samples were mounted in an epoxy and metallographically polished. The microstructure was examined using a scanning electron microscope (SEM, S-2500; Hitachi). The compositions of the reaction products were analyzed using an energy-dispersive X-ray spectrum (EDS). The shear strength of junctions was tested by Condor 150 tester made by XYZTEC Company. The reported values are average results of at least five measurements at different regions.

3. Results and discussions

3.1. Interfacial evolution analysis of p-type graded TE arm

Solder paste SAC305 was firstly coated on the fine polished surface of p-type $Bi_{0.5}Sb_{1.5}Te_3$ by stencil printing and maintained at 255 °C for 30 s. However, poor wettability between SAC305 and bare $Bi_{0.5}Sb_{1.5}Te_3$ was found. Based on our preliminary work [13], to improve the wettability between SAC305 and TE materials, Ni was sputtered on the surface of $Bi_{0.5}Sb_{1.5}Te_3$ by magnetron sputtering. SAC305 was then printed on the surface of Ni coating and used to connect medium-temperature $AgSbTe_{2.01}$. Junction microstructure of p-type $AgSbTe_{2.01}/Bi_{0.5}Sb_{1.5}Te_3$ arm was shown in Fig. 2. As shown in the figure, fine connection presented at SAC305/Ni/$Bi_{0.5}Sb_{1.5}Te_3$ interface while expected connection at SAC305/316 stainless steel/$AgSbTe_{2.01}$ interface failed completely. It was founded, in the experiments, $AgSbTe_{2.01}$ bulks would be jacked up inevitably due to the surface tension of the solder during welding process. Certain pressure performed on the top of $AgSbTe_{2.01}$ bulks

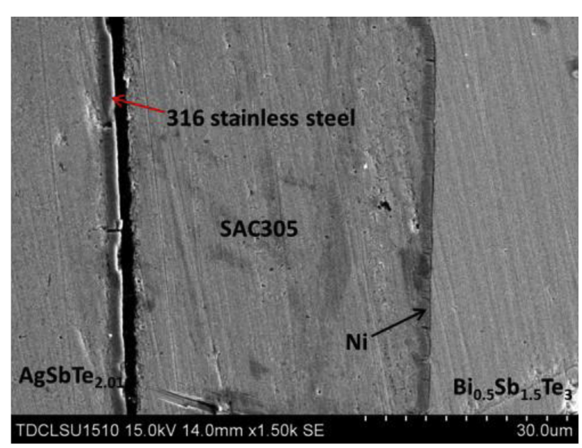

Fig. 2. Microstructure of the joints in p-type TE arm taken SAC305 as solder paste.