Energy Conversion and Management 98 (2015) 134–137

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Silver as a highly effective bonding layer for lead telluride thermoelectric modules assembled by rapid hot-pressing

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ARTICLE INFO

Article history:
Received 19 August 2014
Accepted 23 March 2015
Available online 10 April 2015

Keywords:
Rapid hot-pressing
Thermoelectric material
Intermetallic compounds
Thermal stability

ABSTRACT

We use the rapid hot-pressing method to bond Ag foil onto pure PbTe in order to assess its effectiveness as a bonding layer material for thermoelectric module applications. Scanning electron microscopy and X-ray diffraction are employed to examine intermetallic compound formation and microstructure evolution during isothermal aging at 400 °C and 550 °C. We find that Ag is a promising bonding material for PbTe modules operating at $T_{Hot} \leqslant 400$ °C. Additionally, our approach highlights a highly effective and inexpensive method to metallize PbTe prior to module assembly.

1. Introduction

Thermoelectric power generation, based on the Seebeck effect, is renewable and has negligible carbon footprint. Consequently it has attracted an increasing amount of attention. Thermoelectric power generation modules designed to convert industrial or automotive waste heat into electrical energy, can provide a sizable energy output from the waste heat. Hence, high-efficiency bulk thermoelectric materials have been intensively developed worldwide over the past decade. For some of these materials the dimensionless thermoelectric figure of merit (zT), approaches $zT \sim 2$, which can translate to 20% of Carnot efficiency when incorporated into a device [1,2]. Even though significant progress has been attained in the development of high efficiency thermoelectric compounds, the development of thermoelectric modules to take advantage of these materials has not been as rapid. So far, only low-temperature (<200 °C) thermoelectric materials, such as Bi_2Te_3-based alloys, have been widely developed and incorporated in commercial cooling or heating devices [3–6]. Mid-temperature (200–600 °C) PbTe-based thermoelectric devices assembled by high temperature fabrication processes, such as brazing or diffusion bonding, have lower yields and fierce diffusion problems that degrade thermoelectric performance and show poor adhesion during long-term service [7–10]. A similar situation exists in the case of $CoSb_3$-based thermoelectric devices [11].

The use of a bonding layer, inserted between the thermoelectric component and the electrode, is needed for low electrical and thermal contact resistance. The objective of this study is to develop appropriate bonding materials that will allow reliable long-term operation in PbTe-based thermoelectric modules [12–14]. According to the vertical section of the AgPbTe ternary phase diagram [15], Ag could react with PbTe to form Ag_2Te intermetallic compound. Many recent works have reported the good thermoelectric properties of Ag_2Te itself, and furthermore, Ag also enhances the performance of PbTe [16–20]. Silver is known to be soluble in PbTe with significant temperature dependence. This temperature dependence of Ag, in metal rich PbTe results in n-type doping from interstitial Ag, which leads to a temperature dependence of the n-type dopant concentration. In Te rich p-type samples, the Ag likely fills Pb vacancies, donating electrons, but also replaces some additional Pb acting as acceptor, as well as donating electrons when Ag goes to interstitial positions [18,21]. Additionally, the coefficient of thermal expansion (CTE) of Ag is 18.9×10^{-6}/K, very close to that of PbTe (20.4×10^{-6}/K) [22,23]. This small difference will reduce potential reliability issues arising from the CTE mismatch. Hence, Ag is chosen as the bonding material in this work because of its good electrical and thermal conductivity, and low CTE mismatch. Issues relating to the identification of intermetallic compounds, microstructure evolution during mid-temperature operation and

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http://dx.doi.org/10.1016/j.enconman.2015.03.089
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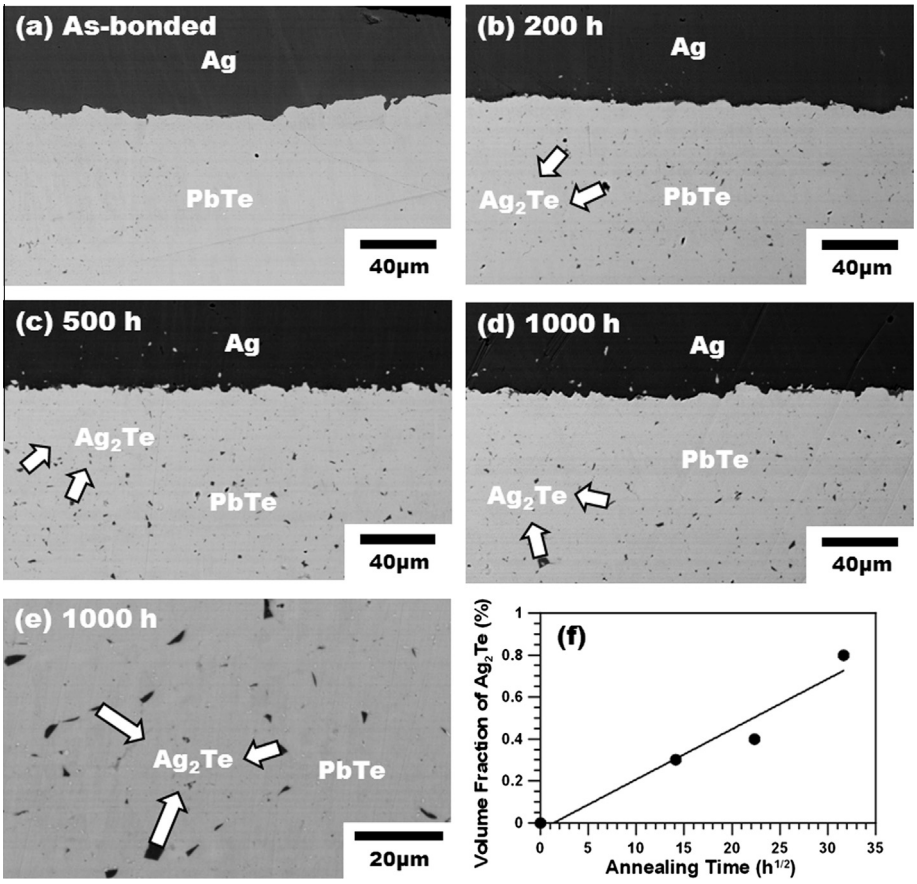

Fig. 1. Interfaces of Ag/PbTe/Ag after aging at 400 °C for (a) 0, (b) 200, (c) 500 and (d) 1000 h. (e) Zoom-in view for the PbTe region of (d). (f) Volume fraction of Ag_2Te as a function of square root of the annealing time.

thermoelectric behavior will be also be discussed. This work should provide the foundation for building thermoelectric modules for power generating which require long-term operations at high temperature.

2. Experimental

In this study, stoichiometric PbTe ingots were prepared by melting Pb (99.999%) and Te (99.999%) in an evacuated and sealed quartz tube at 1000 °C for 6 h, followed by annealing at 700 °C for 48 h to ensure the homogeneity. The resulting PbTe ingots were then ground into powders by ball milling in Ar atmosphere for 1 h. The mean particle size (diameter) of PbTe powders after milling was 8.5 ± 2.1 μm. Silver foil (99.9%) with a thickness of 127 μm was polished using an 800 grit SiC sandpaper and then cleaned with acetone in an ultrasonic bath. After the Ag foil had been cleaned, 4 g of PbTe powder were placed between two polished Ag foils inside a graphite die to produce a disk 3 mm thick with diameter of 12 mm. The resulting Ag/PbTe/Ag structure was subsequently placed in a hot press, in which it was bonded and sintered for 3 h under Ar flow. The bonding pressure and temperature were 40 MPa and 550 °C, respectively. Finally, the samples were retrieved and isothermally annealed at 400 °C and 550 °C. Following each annealing process, the samples were mounted in epoxy resin, and metallurgically polished. The Seebeck coefficient [24], and thermal diffusivity (Netzsch LFA 457) were measured along the pressing direction as appropriate for its intended use. The thermal conductivity for each sample was calculated using the relation $\kappa = DdC_p$, with D being the measured diffusivity, d the sample density, and C_p the heat capacity at constant pressure. The density used in the calculation was the measured density at

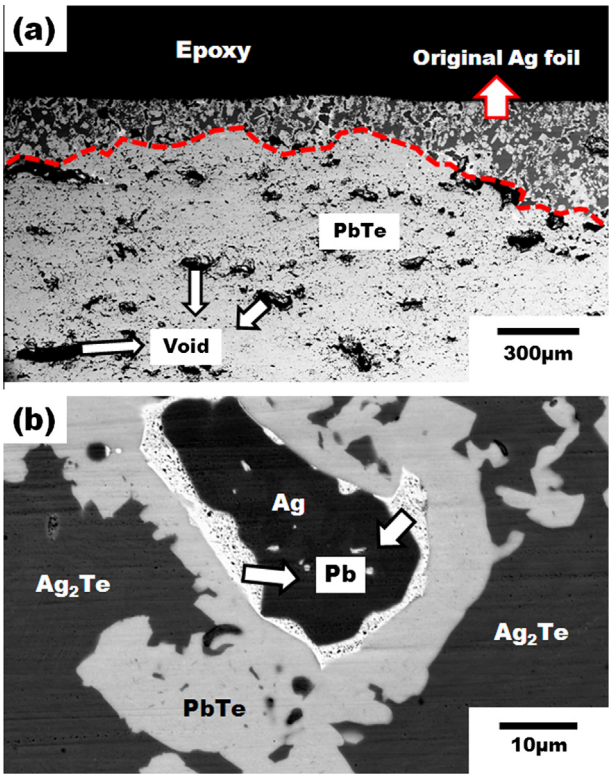

Fig. 2. Micrographs of Ag/PbTe/Ag after aging at 550 °C for 50 h. (a) Low magnification view showing the Ag foil had disappeared. (b) Zoom-in view showing the co-existence of the reactants and the reaction products.