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One-step bonding of Ni electrode to *n*-type PbTe — A step towards fabrication of thermoelectric generators

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ABSTRACT

PbTe-based thermoelectric materials are good candidates for harvesting waste heat at mid-range temperatures due to their high thermoelectric efficiencies. Excellent quality and reliability of the bonding between the thermoelectric material and the electrode at high temperatures are essential for manufacturing thermoelectric generators. Here, a technique has been developed to achieve high-quality bonding between PbTe and the electrode. We have successfully performed one-step sintering of nickel electrode to *n*-type PbTe powder using spark plasma sintering. The fabricated interphase, composed of nickel telluride, is continuous and homogeneous across the junction, without visible flaws on the electrode or in the interphase and PbTe. To evaluate the long-term thermal stability of the fabricated bond, an aging test was conducted at 823 K for 360 h under vacuum. The microstructures and chemical composition of the fabricated bonding and the aged sample were investigated in detail by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy analysis. No excess reaction was observed between the electrode and the thermoelectric material after aging, supporting the formation of a chemically stable interphase, which acts as a diffusion barrier. Degradation of the PbTe was detected after aging, however. The fabricated interface meets the required criteria for maximum efficiency of PbTe materials.

1. Introduction

Lead chalcogenides are known for their high thermoelectric performance in both *n*-type [1–3] and *p*-type [4–6] compounds at temperatures ranging from 500 K to 900 K. This makes them excellent choices as materials for solid-state thermoelectric generators designed for harvesting waste heat [7]. PbTe-based materials have been used in radioisotope thermoelectric generators (RTGs) [8] and more recently, in terrestrial applications [9] due to the latest improvements in their thermoelectric figure of merit (zT). Nevertheless, a thermoelectric generator not only bases its performance efficiency on the high thermoelectric efficiency (zT) of its p and n couples, but also on good contacts with the electrodes [10]. Thermoelectric materials are joined to metal electrodes either through direct reaction [11] or by fabricating intermediate layers as diffusion barriers [12]. In either case, the obtained interphases are required to: (i) inhibit continuous reaction between the thermoelectric materials and the electrodes [13]; (ii) provide mechanical stability with no major defects or fractures [12]; (iii) have low thermal resistance [14]; and (iv) create ohmic contacts with low electrical resistance to eliminate voltage thresholds at the junction, which can diminish the total performance of the generator [15].

One of the major challenges is the choice of electrical contact (electrode), which should have minimum thermal mismatch with the thermoelectric material at the generator's working temperatures [16]. To maintain a reliable and lasting mechanical bond and to meet expectations of generator performance, comparable coefficients of thermal expansion (CTE) are essential for the thermoelectric material, the electrode, and any interphase that is formed [17]. Lead telluride is known for its high CTE, 20×10^{-6}/K, when compared to the metals (Ni, Fe) commonly used as electrodes. This makes it more difficult to bond PbTe to an electrode due to the stress caused by thermal expansion [18]. Nevertheless, Ni (CTE $= 13.4 \times 10^{-6}$/K) and Fe (CTE $= 11.8 \times 10^{-6}$/K) were studied as electrode materials for PbTe [11,19]. The Fe/PbTe joint was found to be successful for *n*-type material, revealed as a mechanically stable joint with a low electrical resistance at the junction [19]. Temperatures as high as 1073 K were employed to form the Fe/PbTe joint [20], however, which might damage the PbTe. Nickel was joined to PbTe thermoelectric material by plasma activated sintering for the first time by Orihashi et al. [21], and the joint showed low electrical resistance at the contacts. Recently, in a study by Xia et al. [11], the same elements were bonded by a one-step hot press process, simultaneously consolidating and bonding the thermoelectric material to the electrode, and the detailed microstructures and composition of the interface were reported. It appears that Ni is a more viable electrode for PbTe than Fe.

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Various approaches have been employed to create an effective diffusion barrier (interphase) between the thermoelectric material and the electrode, such as metallic thin film deposition [12,22], soldering [23], brazing [24], and metallization processes [11,25]. Recently, fabrication of bulk thermoelectric materials by the spark plasma sintering (SPS) technique has become more popular due to the fast sintering of high-quality dense products [26]. This technique has also been employed to bond electrodes to skutterudite [27,28] or magnesium silicide based thermoelectric materials [25]. In this study, one-step bonding of *n*-type PbTe to high purity Ni plate was achieved by SPS. The chemical composition and microstructures at the interface were investigated in detail. We demonstrate a homogeneous interphase between the Ni electrode and the *n*-type PbTe. The thermal stability of the interphase and the thermoelectric material were also studied by aging the assembly at 823 K for 360 h.

2. Materials and methods

Polycrystalline $PbTe_{0.9988}I_{0.0012}$ was synthesized by mixing stoichiometric quantities of high purity Pb (99.999%), Te (99.999%), and PbI_2 in vacuum-sealed quartz ampoules and then heat-treating them at 1373 K for 10 h. The samples were quenched in cold water, followed by annealing at 823 K for 72 h. The obtained *n*-type lead telluride ingots were hand ground to a fine powder in a protective atmosphere. The powder (Fig. 1(a)), consists of particles under 10 μm in size with a random distribution. The obtained powder was sintered into 12 mm diameter disk-shaped pellets using spark plasma sintering (SPS) at 793 K and axial pressure of 40 MPa for 30 min.

The laser flash method (Linseis LFA 1000) was used to measure the thermal diffusivity (D_T). The thermal conductivity was calculated from $k=\rho DTc_p$, where the density (ρ) was calculated using the measured weight and dimensions. The specific heat capacity (C_p) was estimated by $c_p=3.07+4.7\times10^{-4}\times(T[K]-300)$. The electrical resistivity and Seebeck coefficient were measured using a Linseis LSR-3 instrument.

In order to sinter the PbTe powder to the Ni plate, a disk-shaped nickel plate with a thickness of 500 μm was polished to 1 μm surface roughness and ultrasonically cleaned with ethanol to remove possible contaminants on the surface. Subsequently, 1 g of PbTe powder was assembled with the Ni plate in a 12 mm graphite die. Fig. 1(b) illustrates the layered structure of the assembly. The temperature was measured with a thermocouple located inside the bottom punch, close to the surface of the nickel plate. Graphite foil was used between the die, punches, and assembly to improve thermal contact and force distribution. The consolidation of the assembly was carried out by SPS at 773 K, 793 K, and 873 K, with uniaxial pressure of 40 MPa for 10 min under vacuum. Heating and cooling rates of 5 K/min were used.

The chemical composition and crystallographic structure of the reaction product between PbTe and Ni was characterized by X-ray diffraction (XRD) on a GBC MMA using Cu Kα radiation (λ = 1.544 Å, 40 kV, 25 mA). In order to investigate the microstructure and determine phases, the sample was prepared for electron back-scattering diffraction (EBSD) by manual grinding down to 12.3 μm, followed by cross-sectional ion milling on a Leica TIC-020.

EBSD and energy dispersive X-ray spectroscopy (EDS) information was obtained simultaneously from a 80 × 60 μm^2 area using a JEOL JSM-7001F field emission gun-scanning electron microscope (SEM) operating at 15 kV accelerating voltage, ~5.5 nA probe current, and 1500× magnification. The microscope was fitted with a Nordlys-II EBSD detector and an 80 mm^2 X-Max EDS detector interfacing with the Oxford Instruments Aztec software suite. The EBSD mapping conditions were optimised beforehand with 44, 42, and 40 reflectors employed for the Ni, Ni_3Te_2, and PbTe phases, respectively, as well as 4 × 4 binning, 2 background frames, a Hough resolution of 50, and concurrently indexed individual Kikuchi patterns up to 8 bands after preliminary EDS identification of the phases using TruPhase. The raw EBSD map returned an overall indexing rate of 98.65%, such that the zero solutions were concentrated at (sub)grain boundaries or phase interfaces. The map step size of 0.095 μm that was employed was equivalent to an EDS map resolution of ~2048 × 2048 pixels. Other EDS-based settings included a 20 keV energy range, auto-selection of the number of channels, a process time of 3 and a detector dead time of ~55–60%.

Thermoelectric modules for power generation are commonly encapsulated in inert atmosphere or under vacuum [8,29]. In order to assess the thermal stability of the joints, PbTe/Ni samples were heat-treated at 823 K for 360 h in a vacuum-sealed quartz tube. The microstructure analysis was also carried out for the heat-treated samples.

3. Results and discussion

Fig. 2(a) and (b) shows the thermoelectric transport properties of the fabricated *n*-type PbTe. These values are consistent with previous studies [1,30] for *n*-type PbTe, indicating a thermoelectric figure of merit of roughly 1.2 at 700 K for a heavily doped compound.

The back-scattered electron (BSE) micrograph in Fig. 3(a) presents the entire cross section of the Ni plate and *n*-type PbTe interface, which were bonded at 793 K for 10 min. A continuous diffusion barrier layer is formed between the PbTe and the Ni along the roughly 10 mm length of the assembly. We can observe dense lead telluride without visible cracks, major porosity, or defects, as opposed to the interface with PbTe that was directly hot pressed to Ni [19], where cracks were observed in the nickel electrode.

Fig. 3(b) and its inset show higher magnification micrographs of the bonding region, confirming the good cohesion between the PbTe, the interphase, and its Ni counterpart, with a homogeneous and smooth diffusion layer. The thickness of the interphase, shown in the inset of Fig. 3(b), as measured from the SEM image, is approximately 27 μm.

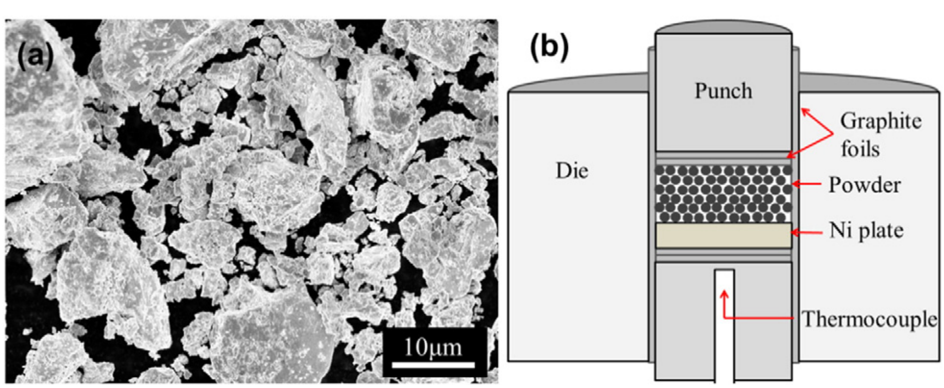

Fig. 1. (a) SEM micrograph of hand-ground *n*-type PbTe fine powder, showing particles smaller than 10 μm; (b) schematic illustration of the experimental set-up in SPS.