Application of Spark Plasma Sintering for Manufacturing of Thermoelectric Materials

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Abstract

V-VI thermoelectric compounds like Bi_2Te_3-based alloys are well known for room temperature applications like Peltier coolers or thermogenerators. Their anisotropic physical properties and mechanical weakness are a problem for the manufacturing. To overcome the mechanical problem Spark Plasma Sintering (SPS) was used. 2 inch Wafers of polycrystalline bismuth telluride based n-type and p-type thermoelectric materials were successfully fabricated through SPS-technique, starting from commercially available zone-melted ingots.

This paper will report on the milling technique and the influence of the SPS process on the microstructure, the thermoelectric and mechanical properties of the polycrystalline materials. A preferentially oriented microstructure was formed keeping the high quality of the the starting material. Through the polycrystalline structure, the bending strength of the sintered material was increased about three times compared with coarse crystalline ingots.

Introduction

Bismuth telluride based materials are widely used for thermoelectric devices in the range 200 – 400 K. The materials exhibit a remarkable anisotropy of their physical properties. The thermoelectric properties of these alloys along the crystallographic a-axis is superior to that in c-axis, which originates from the layered structure with rhombohedral symmetry. Unidirectional crystal growth methods, such as Bridgman method, THM method etc. are commonly used for their preparation [1-4]. Although the resulting single crystalline or coarse crystalline materials present excellent thermoelectric properties, they have poor fracture toughness due to weak Van der Waals bonding between Te containing layers [5, 6]. Powder metallurgical methods, which produce statistically orientated polycrystalline microstructure and grain strengthening effect to avoid the incidental cleavage failure, are intensively studied [5-8]. However, conventional powder metallurgical methods need to produce the ingot (to get homogeneous distribution of all main elements and dopants), pulverizing the ingot and sinter it. Spark Plasma Sintering (SPS) is a short time consolidation technique, which enables rapid sintering and synthesis of various materials (metals, ceramics and composites) applying dc current pulses with several hundred or thousand ampere while mechanical pressure is applied. SPS is postulated to generate sparks between powder particles due to the pulsed current [9]. The effects caused by the spark plasma sintering are not yet understood clearly. However, our experimental results show the activating effect of the pulsed current [10, 11].

Traditional methods use high-energy milling or mechanical alloying for the Spark Plasma preparation of thermoelectric powders based on Bi_2Te_3 starting from the elements [12-15]. Thermoelectric and mechanical properties vary in literature from below average to superior, but the samples size is too small for the use of commercial production methods which requires typically 2 inch wafers (2 mm in height). For the powderization of zone melted ingots, planetary ball mills or manual grinding methods are used. The resulting powders show high sinterability because of their large specific surface but often broadened XRD diffraction peaks beginning amorphization and with short sintering high defect concentrations.

For the preparation of textured materials without long sintering times, the texture of the starting materials can be used. To do this, the powderiziation process has to be cold and fast.

Experimental details

Commercially available rod-shaped ingots of n- and p-type alloys based on Bi_2Te_3 were used as starting material (Peltron GmbH, Fürth, Germany). The nominal composition is $Bi_2Se_{0.25}Te_{0.75}$ for the n-type and $Bi_{0.5}Sb_{1.5}Te_3$ for the p-type alloy. The ingots were pulverized by using a high-speed rotor mill (Pulverisette 14, Fritsch GmbH) und sieved to a particle size < 100 μm. Subsequently, the powders was consolidated by spark plasma sintering (HP D 250, FCT Systeme GmbH) under a pressure of 20-50 MPa using graphite dies with 45 mm inner diameter. The heating rate was adjusted to 100 K/min, the temperature measurement was done with K-type thermocouples in the die. To avoid high forces while removing the sinterbodies from the pressing tool, additional graphite and metal foils were used. The density was determined by Archimedes' method. For the mechanical testing by 3-point bending tests, "single-crystalline" samples were cut by electro-discharge machining into bending bars (35 mm in length, 5 mm width, 15 mm load span). The sintered samples for the tests were cuted with a diamond wire saw. Mechanical testing was done with Zwick UPM 1476 equipment. Observations of fracture surfaces and metallographic samples were carried out by using Zeiss Evo 50 scanning electron microscope. The Seebeck coefficient and the electrical conductivity were measured with the IPM-SR2, built at the Fraunhofer-IPM with specimen typically 15 mm x 3 mm x 1.5 mm in size [16]. The Seebeck coefficient is measured with a temperature gradient about 1-3 K, that can be reversed. The electrical conductivity is measured with three different currents ranging from 10 to 50 mA. Specific heat capacity and thermal diffusivity were determined with Netzsch GmbH NanoFlash LFA 447 on quadratic samples with 15 mm length and 2 mm in thickness.

Results and Discussion

The starting material was characterized before crushing. The wafers were cuted from the zone melted ingots with basal planes perpendicular to the c-axis. The results measured at 300 K show a good homogeneity of the thermoelectric properties with values between 172-225 mV/K for n-type material and 203-240 mV/K for p-type alloy respectively. Together with the electric conductivity, the power factor can be calculated to an average value of 14 $\mu W/K^2cm$ for n-type material and 23 $\mu W/K^2cm$ (300 K). Fig. 1 shows the morphology of the powdered alloy. The single particles have flake-shaped form with pronounced anisotropy. The edge of the flaks is typically between 20 and 100 μm, the thickness is about 20 micron. The weak bonding between the atomic layers of the crystal structure divides the coarse crystalline ingots privileged perpendicular to the c-axis. So typically the shortest edge of the flake (perpendicular to the basal plane) is in [00l] direction. XRD analysis confirmed this orientation in the flakes. Due to the particle shape, the powders arrange in preferred direction when poured into the pressing mould. The basal plane of the flakes is parallel to the bottom of the mold and the c-axis parallel to pressing direction.

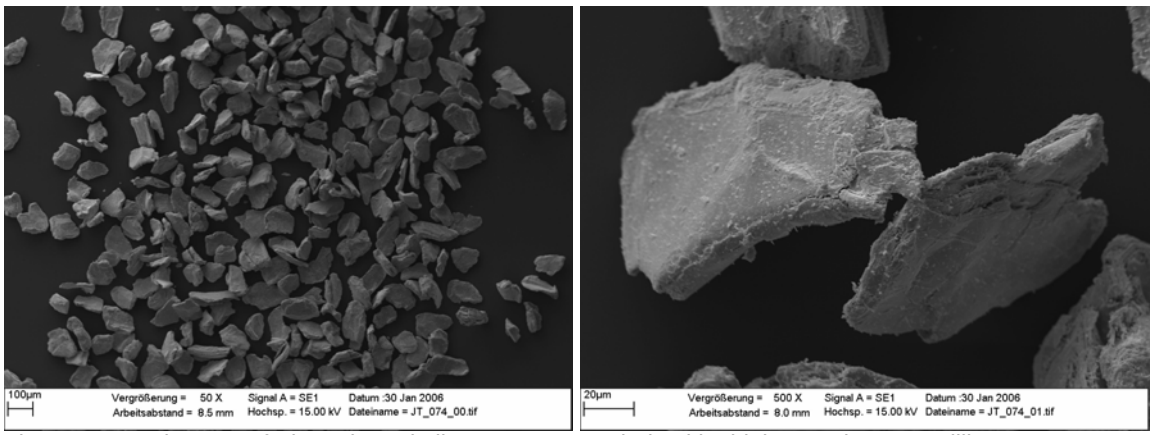

Figure 1: SEM images of Bi_2Te_3-based alloy powers, powderized by high-speed rotory milling.

Figure 2 (left) show the development of the density depending on the sintering temperature for both alloy- types. Sintering was done with a pressing force of 22 MPa. The sinterability of the p-type alloy is better than that for the n-type. Complete densification for n-type and p-type

alloy can be reached with higher pressing forces. Best condition for the spark plasma sintering are 400°C/1 min dwell (n-type) and 375°C/0 min dwell (p-type) at 35 MPa.
During the sintering, no changes in the composition are detectable by XRPD, surface area EDX or elemental analysis by emission spectroscopy.

The thermoelectric properties of the sintered samples were measured parallel to the pressing direction. Depending on the sintering temperature, the Seebeck coefficients at 300 K are between -142 μV/K and -202 μV/K for n-type material and between 165 μV/K and 240 μV/K for p-type respectively. The power factors ranging from 6-18 $\mu W/K^2cm$ (n-type) to 11-39 $\mu W/K^2cm$ (p-type). Figure 2 (right) show the effect of the sintering temperature to the thermoelectric power factor as a function of the sintering temperature for the p-type alloy. The power factor, which contains electrical conductivity and Seebeck coefficient only, is less sensitive to the variation of the sintered density than the figure of merit, which contains the thermal conductivityas demoninator . The results show that the powderization and the spark plasma sintering have no negative influence on the thermoelectric properties.

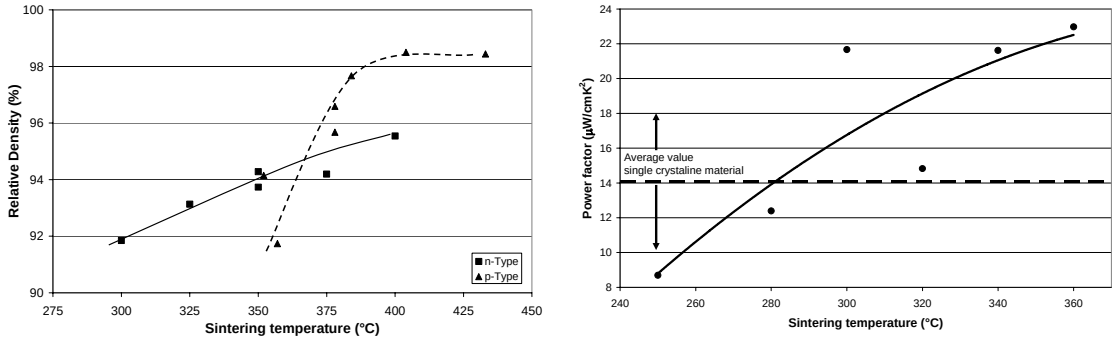

Figure 2: Development of the sintered density with the sintering temperature for both alloys (left). The dependence of the power factor for sintered samples (p-type) for different sintering temperatures is shown on the right.

The samples show anisotropic physical properties in terms of thermal (λ) and electrical conductivity (σ), Seebeck coefficient (S) and dimensionless figure of merit (ZT), shown in Figure 3. The direction of the better thermoelectric properties is perpendicular to the pressing direction as expected [17].

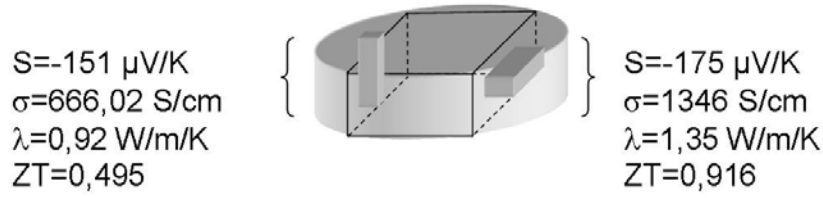

Figure 3: Results of the anisotropic characterization of the physical properties of a spark plasma sintered sample (n-type alloy).

The mechanical properties of the sintered samples are different to typical commercial crystalline ingots. The mechanical properties were measured by a 3-point bending test method. The loading direction was along the pressing direction of the spark plasma sintered samples and the crystal growth direction for the ingots, respectively. The coarse crystalline ingots show maximum values of the ultimate strength up to 20 MPa, which are in good agreement to typical literature data of about 10 +/-5 MPa [18]. The bending strength of the spark plasma sintered material achieved about 60 MPa (Figure 4). The ultimate strain and the ultimate strength increases with increasing sintering temperature. Due to the fine grain size of the polycrystalline sinterbodies and the good grain-to-grain bonding in the microstructure, the mechanical strength is enormously improved (Fig. 5). It is believed that

the mechanical strength improve the reliability for applications in miniature thermoelectric modules.

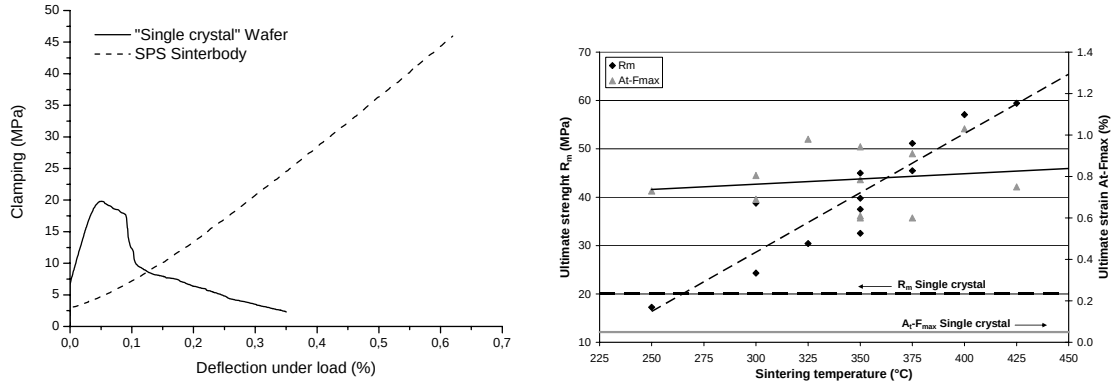

Figure 4: Representative results of 3-point bending tests for coarse crystalline and sintered samples of p-type $Bi_{0.5}Sb_{1.5}Te_3$ (left). The dependence of the ultimate strain and the ultimate strength with the sintering temperature is shown on the right.

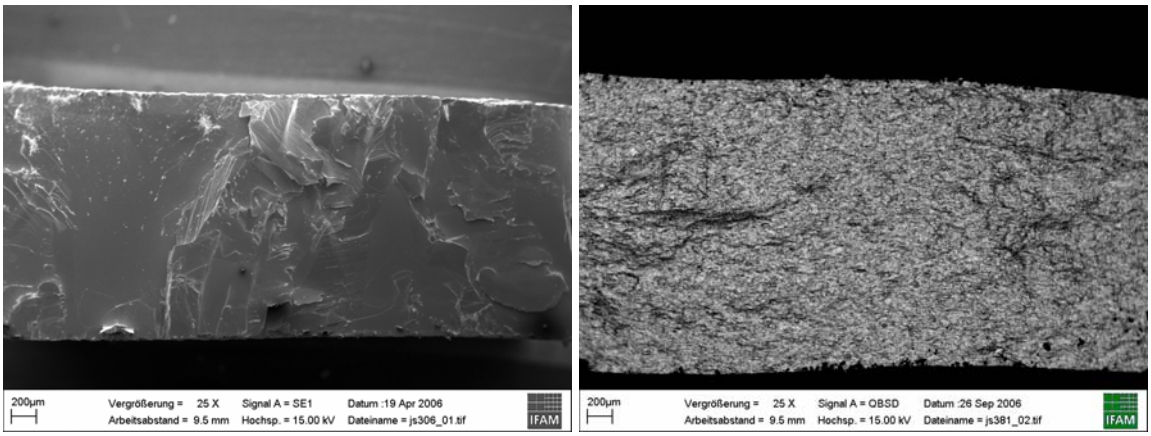

Figure 5: SEM micrographs of the fracture surfaces of 3-point bending bars after mechanical testing. Left: coarse crystalline ingot; Right: Spark plasma sintered powder (400°C/ 1min).

Conclusions

By using a suitable powderization and sintering process, the mechanical properties of sintered samples of n-type and p-type alloys based on Bi_2Te_3 have been improved keeping the original thermoelectric properties. In the range of the measuring error, the thermoelectric properties have not changed while powder metallurgical processing. The developed technology allows the production of polycrystalline thermoelectric materials for commercial applications. The fine grain size of the microstructure increases the bending strength of the sintered samples to maximum values of 60 MPa, which corresponded to more than 250% of that of the zone-melted, coarse crystalline material with the same composition. Due to the superior mechanical properties, the handling is easier and the typically small yield caused by the defects induced during manufacturing might be overcome.

Acknowledgements

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