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Optimization of hot-press conditions of Zn_4Sb_3 for high thermoelectric performance. II. Mechanical properties

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Abstract

Mechanical properties including Young's modulus, Vickers hardness, 3-point bending strength, and fracture toughness, were evaluated for p-type semiconductive thermoelectric Zn_4Sb_3 hot-pressed at four different temperatures ranging from 738 K to 753 K in order to study the effect of sintering temperature. Young's modulus increased linearly from 58 GPa to 76 GPa with increasing sintering temperature. The hardness exhibited a similar proportional relation, ranging from 1.4 GPa to 1.6 GPa. The bending strength and fracture toughness were 56–70 MPa and 0.64–0.7 MN $m^{-3/2}$, respectively. Based on experimental data, the anticipated thermal stress was estimated for a Zn_4Sb_3 component assembled in a thermoelectric power generator.

Keywords: Intermetallic; Semiconductor; Powder metallurgy; Elasticity; Strain

1. Introduction

Recently, p-type semiconductive ε-Zn_4Sb_3 has attracted much attention in relation to thermoelectric application [1,2], because of its excellent performance as a p-leg component of a thermoelectric generator (TEG). The compound has a high figure of merit: ZT = 1.3 at 673 K [1,2], where ZT is defined as $ZT = \alpha^2\sigma T/\kappa$, with α, σ, T and κ representing the Seebeck coefficient, electric conductivity, absolute temperature and thermal conductivity, respectively. Among the fabrication methods for the Zn_4Sb_3 material, the most attractive is hot pressing, because it provides pore-free specimens with better transport properties and benefits from the view of commercial production. In previous work [3], we have studied the effects on the thermoelectric performance of ε-Zn_4Sb_3 of different hot-pressing conditions, including sintering temperature, time, and atmosphere, and found that the optimum sintering temperature was 748 K. Only the Zn_4Sb_3 specimen fabricated at this temperature in vacuum has exhibited a ZT value over 1 at 673 K.

When Zn_4Sb_3 material is used in a TEG device, the temperature difference between the hot and cold ends might lead to a high thermal stress load within the component, in addition to the mechanical stress for good thermal contact between the device and heat source. Thus, the requisite properties for a component of a TEG device include not only high thermoelectric performance but also mechanical durability under the TEG operating conditions.

Many authors have reported on the properties of the ε-Zn_4Sb_3 compound, but most studied the physical properties, especially the transport characteristics. Regarding mechanical properties, Ohzora et al. [4] have reported the bending strength of the material. To the best of our knowledge, however, there is no other research related to the material's mechanical properties except relating to the thermal expansion coefficient [1,2,5].

In a TEG device, the thermoelectric components need to be strongly joined with the electric collecting metals, and thus important mechanical parameters for the ε-Zn_4Sb_3 material include not only strength but also the elastic modulus. The matching of the components thermo-elastic behaviors is critical for stable operation of the TEG device. In particular, when the compound is used as a component in a segment-type

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TEG device [6–8], its mechanical characteristics should be compatible with the other coupled thermoelectric materials such as Bi–Te compounds.

In this study we have fabricated ε-Zn_4Sb_3 specimens by hot pressing at four different temperatures between 738 K and 753 K, and have evaluated the mechanical properties including Young's modulus, Vickers hardness, bending strength and fracture toughness. In addition to these experiments, we considered the mechanical requirements for application of the Zn_4Sb_3 material as a TEG component by performing thermal stress estimation, and herein discuss advances in fracture strength through microstructure control.

2. Experimental

The fabrication procedures are the same as reported previously [3]. Briefly, ε-Zn_4Sb_3 powder with a mean particle size of 19.5 μm (Toshima Manufacturing Co., Higashimatsuyama, Japan), prepared by solid-state reaction of high purity Zn and Sb, was hot-pressed at 738, 743, 748 and 753 K, under uniaxial pressure of 49 MPa for 5 h in vacuum. Pore- and crack-free sintered specimens were obtained after full densification. X-ray diffractometry confirmed the specimens were single-phase ε-Zn_4Sb_3. Table 1 shows the densities and hot-pressing conditions. The sintered specimen was ground at its surface with a diamond wheel, and cut into parallelepipeds with sizes of about 3 mm × 3 mm × 20 mm.

Young's modulus was evaluated by the sound resonance method. Vickers hardness was measured by indentation of a diamond pyramid on the polished surface. To avoid any cracking at the indent corners, the indentation load was fixed at 0.49 N, which left a small indent with a diagonal of less than 25 μm. The indentation was conducted on a single grain larger than 150 μm in order to observe a clear indent without any influence from the grain boundary. Five indentations were carried out for one sample. Bending strength was measured by a 3-point flexural test with a lower span of 16 mm and a crosshead speed of 0.5 mm/min. Five test pieces were tested to get the average value for each temperature. The stressed surface was polished to a mirror plane to avoid the influence of surface defects. Fracture toughness was evaluated by the single edged notched beam (SENB) method with three test pieces for each temperature. The parallelepiped specimen was cut at the center with a thin diamond blade to form a straight notch with a sharp V-shape tip. The relative notch depth, a/W, was 0.27–0.32, where a and W are the notch length and specimen width, respectively. Fracture toughness, K_{IC}, was calculated by the equation [9]:

$$K_{IC} = \frac{3PLYa^{1/2}}{2BW} \tag{1}$$

where P, L, Y and B are the fracture load, lower span, numerical correction factor and specimen thickness, respectively. All measurements were carried out at room temperature.

Table 1
Bulk density and open porosity of hot-pressed ε-Zn_4Sb_3

Sample number	HP temperature[a] (K)	Bulk density (g cm^{-3})	Open porosity (%)
Z1	738	6.20	<0.1
Z2	743	6.40	<0.1
Z3	748	6.41	<0.1
Z4	753	6.30	0.2

[a] Hot-pressing was conducted at these temperatures for 5 h under 49 MPa in vacuum.

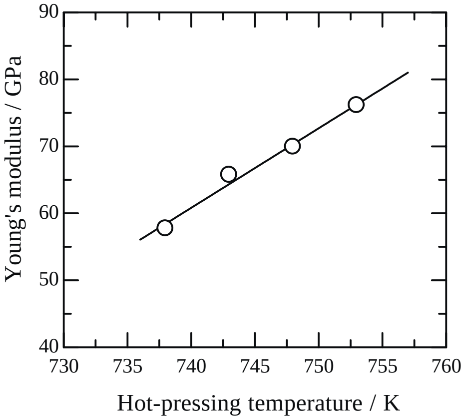

Fig. 1. Young's modulus of ε-Zn_4Sb_3 hot-pressed at various temperatures.

3. Results

Fig. 1 shows the variation of Young's modulus with hot-pressing temperature. Young's modulus increases linearly with increasing sintering temperature, ranging from 57 GPa to 77 GPa. Vicker's hardness also shows a similar tendency (Fig. 2). These results suggest that the higher sintering temperature leads to robust bonding in the Zn_4Sb_3 lattice and fewer crystal defects.

Fig. 3 indicates the bending strength and hot-pressing temperature. The Zn_4Sb_3 specimen failed in a brittle manner with negligible plastic deformation. The average values in-

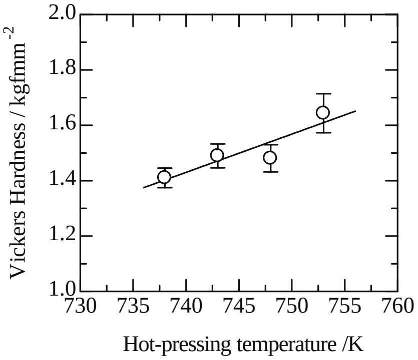

Fig. 2. Vickers hardness of ε-Zn_4Sb_3 hot-pressed at various temperatures.

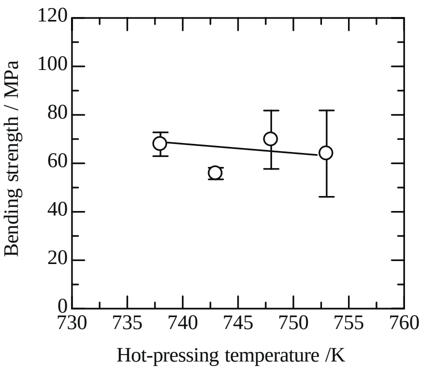

Fig. 3. Bending strength of ε-Zn_4Sb_3 hot-pressed at various temperatures.

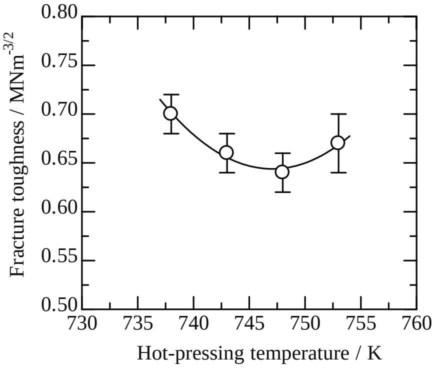

Fig. 4. Fracture toughness of ε-Zn_4Sb_3 hot-pressed at various temperatures.

dicate a slight degradation with increasing sintering temperature, ranging between 60 MPa and 80 MPa. Fracture toughness of Zn_4Sb_3 ranged from 0.65 MN $m^{-3/2}$ to 0.7 MN $m^{-3/2}$ (Fig. 4). Values decreased with increasing sintering temperature up to 748 K, then increased for the specimen at 753 K. This temperature-dependency is the reverse of that for bulk density as reported in our previous paper [3]. The relationship between the bulk density and fracture toughness for Zn_4Sb_3 materials is shown in Fig. 5, indicating an inverse proportional correlation between them, the meaning of which is not clear at the present time.

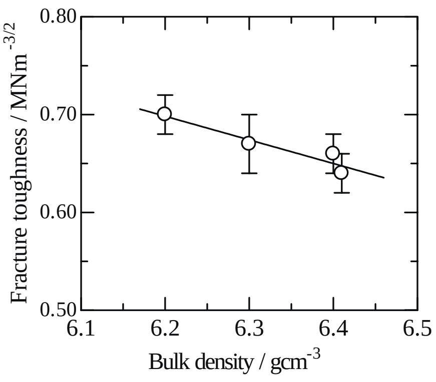

Fig. 5. The relation between bulk density and fracture toughness for ε-Zn_4Sb_3 hot-pressed at different temperatures.

4. Discussion

In the present work we have evaluated the mechanical properties of semiconductive ε-Zn_4Sb_3 material. From the viewpoint of practical application as a component of a TEG device, it is necessary to evaluate the mechanical durability and compatibility with other device materials. Using the mechanical data, we can estimate how much stress emerges when the material is assembled in a TEG device.

Firstly, we consider the stress occurring through thermal expansion mismatch between Zn_4Sb_3 and a current collector metal. If these materials are firmly joined, the stress in Zn_4Sb_3 which accompanies a temperature change is expressed as follows [10]:

$$\sigma_z = E_z(\alpha_m - \alpha_z)\,\Delta T \qquad (2)$$

where σ, α, and ΔT are the stress, thermal expansion coefficient and temperature difference, respectively, and z and m designate the Zn_4Sb_3 and current collector metal, respectively. When the collector metal is nickel and is joined with Zn_4Sb_3 during hot-pressing, the estimated tensile stress in Zn_4Sb_3 (Specimen Z3) is 140 MPa, using α_z and α_m of $18.3 \times 10^{-6}\,K^{-1}$ [11] and $13.8 \times 10^{-6}\,K^{-1}$ [12], respectively, and $\Delta T = 400$ K. The stress is almost two times higher than the mean fracture strength of Zn_4Sb_3; hence the component may well be damaged at an early stage of operation, or even during cooling after hot pressing.

The stress which occurs through thermal expansion mismatch can, however, be suppressed by selecting an adequate metal with $\alpha_m \approx \alpha_z$, but it is difficult to avoid the thermal stress caused by the temperature difference between the hot surface and the inner part of the Zn_4Sb_3 component. In this case, the thermal stress is expressed as [10]:

$$\sigma_z = \frac{E_z \alpha_z\,\Delta T}{1-\mu} \qquad (3)$$

where μ is Poisson's ratio. This model is applicable when the Zn_4Sb_3 component is heated rapidly from a heat source while the inside is still cold. The low thermal conductivity of Zn_4Sb_3, comparable to that of glass, may easily cause such a temperature difference. Poisson's ratio is calculated to be 0.247 from longitudinal and transverse sound velocities [2]. Assuming that ΔT is 100 K, the thermal stress in Zn_4Sb_3 (Specimen Z3) is estimated to be 172 MPa; two times higher than its strength.

These two fundamental simulations reveal that the strength of the measured Zn_4Sb_3, less than 70 MPa, is obviously insufficient as a thermoelectric material for TEG, and should be improved. There are two possible routes to improve the strength of Zn_4Sb_3. The first is to use starting material Zn_4Sb_3 powder with a smaller particle size. The fast fracture strength of brittle polycrystalline materials such as intermetallic alloys and ceramics is known to predominantly depend on the grain size as long as the material is pore- and flaw-free and the lattice bonding strength and fracture toughness are the same. The relation between the strength and grain size is known empirically as the Orowon relation and is expressed as follows [10]:

$$\sigma = \frac{k}{d^{1/2}} \tag{4}$$

where σ, and d are the material's strength and grain size, respectively, and k is a constant. The equation is essentially the same as Eq. (1) with $d \approx a$. By entering the experimental data for σ and K_{IC} into equation (1), it is possible to estimate the size of the grain that triggers fast fracture as an initial flaw. Slow-crack growth before unstable fracture is assumed to be negligible because of a high stress-loading rate.

Thus the estimated strength-determining grain size ranges from approximately 20 μm to 50 μm, which covers a major part of the grain size range of the starting Zn_4Sb_3 powder [3]. If we can prepare Zn_4Sb_3 powder smaller than 10 μm, the mean strength is expected to be over 150 MPa, sufficient for the Zn_4Sb_3 component to remain intact under the anticipated stress during operation.

The second possible route to improve Zn_4Sb_3 strength is to enhance K_{IC}, but the toughness is hard to improve because it strongly depends on intrinsic lattice characteristics, which dominate the relaxation phenomenon of stress intensified at a crack tip through mechanisms such as plastic flow or dislocation slipping.

5. Conclusion

Several mechanical properties of the thermoelectric material Zn_4Sb_3 have been evaluated. Young's modulus and Vickers hardness exhibit a linear correlation with hot-pressing temperature, while bending strength and fracture toughness show degradation by high-temperature sintering at 753 K. From the viewpoint of selecting the optimum hot-pressing temperature, specimen Z3, fabricated at 748 K, had the highest strength and a moderate Young's modulus. Specimen Z3 also displayed the best thermoelectric transport characteristics, as reported previously [3]. We conclude that 748 K is the optimum temperature not only from a thermoelectric view but also from a mechanical view, although the material strength is poor at this stage.

ε-Zn_4Sb_3 is a typical brittle material similar to many other intermetallic compounds, and has a low fracture toughness compared to that of glass, resulting in poor strength. The thermal stress anticipated for use of the material as a component in a TEG device possibly exceeds its fracture strength, and thus improving the strength and/or fracture toughness is greatly desired.

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