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Thermoelectric Properties of Cu₂SnSe₃-Based Composites Containing Melt-Spun Cu–Te

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Abstract: In this study, the Cu–Te alloy ribbons containing nanocrystalline structures were prepared by melt spinning (MS), and were composed of Cu_{2–x}Te, Cu₂Te, Cu_{3–x}Te, and CuTe phases. Crystal grains on both sides of the ribbons were uniformly distributed and the grain size of the contact surface was about 400 nm. The Cu–Te powder was incorporated into the Cu₂SnSe₃ powder by the ball milling process and the Cu–Te/Cu₂SnSe₃ thermoelectric composite was prepared by spark plasma sintering (SPS). With the amount of Cu–Te powder increasing, the carrier concentration of the Cu–Te/Cu₂SnSe₃ composite increased, while the carrier mobility and electrical conductivity initially increased and then decreased. Compared to the Seebeck coefficient of the Cu₂SnSe₃ matrix, the Seebeck coefficient of the Cu–Te/Cu₂SnSe₃ samples increased slightly. Moreover, the Cu–Te/Cu₂SnSe₃ composites had lower thermal conductivity and lattice thermal conductivity over the whole temperature range. The lattice thermal conductivity of the 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite achieved the lowest value of 0.22 W/m·K, which was 78% lower than that of the Cu₂SnSe₃ matrix. The maximum figure of merit of the 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite was 0.45 at 700 K.

Keywords: thermoelectric; composites; Cu₂SnSe₃; melt spinning

1. Introduction

With the development of modern society, global energy crisis and environmental pollution are becoming increasingly severe. Thermoelectric materials become increasingly compelling due to their unique advantages in the field of energy materials. Thermoelectric materials not only achieve direct conversion between thermal and electrical energies, but also have good stability [1,2]. However, the figure of merit that characterizes thermoelectric properties is difficult to improve effectively, which leads to the failure of thermoelectric materials in achieving a wide range of applications. It is well known that the figure of merit ZT is defined as $ZT = \alpha^2 \sigma T / \kappa$, where α and σ are the Seebeck coefficients and electrical conductivity of material, respectively; T is the absolute temperature; κ is the sum of lattice thermal conductivity (κ_L) and carrier thermal conductivity (κ_c) of material [3–5]. These parameters are limited by the internal structure of the material, and interact with each other. Therefore, the coordinated development and optimization of various parameters is the most important task for thermoelectric materials.

Cu-based thermoelectric materials have attracted wide attention due to their special crystal structure, relatively high carrier mobility, and low cost. Recently, research on the *p*-type Cu₂SnSe₃ ternary thermoelectric semiconductor has been increasing. Cu₂SnSe₃ is a promising thermoelectric material due to its narrow band gap (0.84 eV) and large carrier effective mass [6,7]. Various doping on the Sb site of Cu₂SnSe₃ have been carried out to improve its thermoelectric properties and some valuable work has been achieved [8–10]. Besides substituting or doping, the introduction of nanophase/matrix interfaces can also enhance phonon scattering and decrease lattice conductivity, thus improving the ZT value of thermoelectric materials. The melt spinning (MS) process has been widely used

in the preparation of various thermoelectric materials, such as PbTe [11,12], $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ [13,14], skutterudite compounds [15,16], AgSbTe_2 [17,18], etc. Previous results show that a large number of finely microstructured and nanoscale grains can be obtained by MS. However, there is little information regarding Cu-based thermoelectric materials involving the MS process.

In this study, Cu–Te ribbons containing a nanocrystalline structure were prepared using the MS process. The Cu–Te powder-containing nanocrystalline structure was introduced into the Cu_2SnSe_3 matrix by ball milling and the Cu–Te/ Cu_2SnSe_3 thermoelectric composites were prepared by spark plasma sintering (SPS). Effects of the Cu–Te nanocrystalline structure on the thermoelectric properties of Cu–Te/ Cu_2SnSe_3 composites were discussed.

2. Experimental Procedures

The element mass of Cu (99.99%) and Te (99.99%) were weighed at a molar ratio of 1.9:1 due to the sublimation of Te. The mixed raw materials were loaded into a quartz tube, and the quartz tube was subjected to high-frequency induction melting furnace. The chamber was evacuated to 5×10^{-3} Pa and the alloys were melted under the protection of high purity argon (99.999%). The Cu–Te master alloy melt was sprayed onto the surface of a copper roller with a linear speed of 25 m/s under a pressure of 0.04 MPa to obtain Cu–Te ribbons-containing nanocrystalline structure. Then the obtained ribbons were ground into fine powder in agate mortar. Cu_2SnSe_3 ingots were synthesized by conventional melting–annealing methods in which the raw materials used were powders with a purity of more than 99.99%. The stoichiometric mixtures of pure elements Cu, Sn, and Se were sealed in evacuated quartz tube at 1273 K for 12 h, followed by annealing at 923 K for 36 h. Then the obtained Cu_2SnSe_3 ingots were ground into fine powder in agate mortar and mixed with Cu–Te powder by ball milling at 300 r/min for 2 h. The weight ratio of balls to powders was ~10:1. Finally, the resulting Cu–Te/ Cu_2SnSe_3 powder was sintered by spark plasma sintering (SPS) process at 693 K for 8 min in a vacuum under 60 MPa.

The density (ρ) of Cu–Te/ Cu_2SnSe_3 composites was tested by the Archimedes method. The densities of Cu–Te/ Cu_2SnSe_3 composites were above 95% of the corresponding theoretical density. X-ray diffraction (D8-ADVANCE, Karlsruhe, Germany) was used to analyze the phase composition of Cu–Te/ Cu_2SnSe_3 composites at a scanning rate of $4^\circ/\text{min}$. The microstructure of Cu–Te/ Cu_2SnSe_3 samples was characterized by scanning electron microscopy (QUANTA FEG250, FEI, Hillsboro, OR USA). The laser thermometer (LFA-457, Netzsch, Selb, Germany) was used to measure the thermal diffusivity of composites with a diameter of 10 mm and a thickness of 1.5 mm. The surfaces of the measured sample were coated with carbon. The thermal conductivity of Cu–Te/ Cu_2SnSe_3 composites was calculated from the $\kappa = \lambda \rho C_p$ formula where λ is the thermal diffusivity of the sample, C_p is the specific heat (estimated according to Dulong–Petit’s law), and ρ is the density of the sample. The electrical conductivity and Seebeck coefficient were determined simultaneously using ZEM-3 equipment (ULVAC-RIKO, Yokohama, Japan). Uncertainty in the electrical conductivity, Seebeck coefficient, and thermal conductivity measurements was at most 5%. The van der Pauw method was used to measure the Hall coefficient R_H of the composites in a self-made equipment. All composites’ measurements were carried out in the temperature range of 300–700 K.

3. Results and Discussion

3.1. XRD Analysis and Microstructure

Figure 1 shows the X-ray diffraction pattern of Cu–Te alloy powder after MS. It can be seen that the Cu–Te alloy after MS consists of the Cu_{2-x}Te , Cu_2Te , $\text{Cu}_{3-x}\text{Te}_2$, and CuTe phase. Figure 2 shows the SEM image of Cu–Te alloy ribbons, with both sides of Cu–Te alloy ribbons depicting a uniform microstructure. The free surface was relatively rough and the grain size was about 800 nm, as shown in Figure 2a,b. On the other hand, the contact surface was smooth and the grain size was about 400 nm, which were smaller than those of the free surface, as shown in Figure 2c,d.

Figure 1. X-ray diffraction pattern of Cu–Te alloy powder.

Figure 2. SEM images of Cu–Te alloy ribbons after MS; (a) free surface, low magnification; (b) free surface, high magnification; (c) contact surface, low magnification; and (d) contact surface, high magnification.

Figure 3 shows the X-ray diffraction patterns of x vol.% Cu–Te/Cu₂SnSe₃ composites ($x = 0, 0.4, 0.8, 1.2$). It can be seen that the diffraction peaks of the Cu–Te/Cu₂SnSe₃ composites were consistent with peaks of the Cu₂SnSe₃ matrix except for the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite. There was a peak at about 30° in the XRD pattern of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ sample. The unknown phase at ~30° was indexed to be Cu–Te phases such as Cu_{2– x} Te, Cu₂Te, and Cu_{3– x} Te₂. The EDS result of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ sample also confirmed the presence of Cu–Te phases, just as shown in Figure 4. Neither the phases in the Cu–Te alloy ribbons nor the new phase were found in other Cu–Te/Cu₂SnSe₃ composites. This was due to the fact that the addition of melt-spun Cu–Te was relatively too low compared to the Cu₂SnSe₃ matrix.

Figure 3. X-ray diffraction patterns of Cu-Te/Cu₂SnSe₃ composites.

Figure 4. SEM image of fracture morphology of (a) Cu₂SnSe₃; (b) 0.4 vol.% Cu-Te/Cu₂SnSe₃; (c) 0.8 vol.% Cu-Te/Cu₂SnSe₃; and (d) 1.2 vol.% Cu-Te/Cu₂SnSe₃.

In order to better show the microstructure of Cu-Te/Cu₂SnSe₃ composites after SPS sintering, SEM for the fracture morphology of composites was carried out. As shown in Figure 4, with the increase in Cu-Te powders, grain growth of the Cu₂SnSe₃ matrix was inhibited significantly and the grain size decreased. Moreover, it can be seen that there were some micro-pores that were ~250 nm in the grain boundaries, which is shown in Figure 5. The formation of micro-pores was possibly attributed to the low melting point phases such as CuTe, etc., in Cu-Te powders, which melted during the sintering process. Previous studies have shown that there is similar micro-porosity in the sintered skutterudites materials, which is beneficial to the improvement of thermoelectric properties due to the

additional long-wavelength phonon scattering [19]. However, when the addition amount of Cu–Te reached 1.2%, an unusual phenomenon of grain growth can be found in the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite, just as shown in Figure 4d. This phenomenon should be related to the aggregation of Cu–Te phases. With the increase of Cu–Te phases, the aggregation of Cu–Te phases was easy to occur. Figure 5 shows the SEM image of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ sample and EDS results. The presence of micro-voids/nanopores in the 1.2 vol.% Cu–Te/Cu₂SnSe₃ sample can also be easily seen. As the melting points of Cu–Te phases are relatively low, the aggregation region of the Cu–Te phases had relatively weak inhibition ability for grain growth in the sintering process. Therefore, grains of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite were relatively coarse and the size of micro-voids was larger accordingly.

Figure 5. SEM images of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ sample and EDS (Energy Dispersive X-ray Spectroscopy) results.

3.2. Electrical Transport Properties

Table 1 lists the electrical transport properties and relative densities of Cu–Te/Cu₂SnSe₃ composites at room temperature. Due to the presence of micro-pores/nanopores, an additional carrier scattering mechanism which preferentially scatters low energy carriers in the Cu–Te/Cu₂SnSe₃ composite can be introduced. With the amount of Cu–Te phases increasing, the carrier concentration of Cu–Te/Cu₂SnSe₃ composites increased. While the carrier mobility and electrical conductivity of Cu–Te/Cu₂SnSe₃ composites first increased and then decreased with the amount of Cu–Te phases increasing. The decrease in carrier mobility and electrical conductivity should be attributed to the large number of large-size vacancies or micro-voids in the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite.

Figure 6 shows the temperature dependence of electrical conductivity for Cu–Te/Cu₂SnSe₃ composites with different volume fraction Cu–Te phases. At high temperature, the electrical conductivity of the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite was even lower than that of the pure Cu₂SnSe₃ matrix. The 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite showed the highest electrical conductivity, and the σ was 2.04×10^3 S/cm at 700 K. This is possibly related to the 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite's higher density.

Table 1. Chemical composition and some physical parameters of x vol.% Cu–Te/Cu₂SnSe₃ composites at room temperature.

x	Hall Coefficient R_H ($10^{-3} \text{ cm}^3/\text{C}$)	Carrier Concentration n (cm^{-3})	Carrier Mobility μ (cm^2/Vs)	Electrical Conductivity σ (S/cm)	Relative Density
0	3.368	1.866×10^{21}	7.14	1.94×10^3	96.2%
0.4	3.550	1.923×10^{21}	7.21	2.04×10^3	95.2%
0.8	9.212	1.990×10^{21}	9.63	2.97×10^3	96.9%
1.2	2.257	2.291×10^{21}	6.16	1.95×10^3	96.3%

Figure 6. Temperature dependence of the electrical conductivity (σ) of Cu–Te/Cu₂SnSe₃ composites.

The temperature dependence of Seebeck's coefficient (α) for the Cu–Te/Cu₂SnSe₃ composite is shown in Figure 7. The Seebeck coefficient of Cu–Te/Cu₂SnSe₃ composites was slightly higher than that of the pure Cu₂SnSe₃ matrix, indicating that the decrease in Seebeck's coefficient caused by carrier concentration was not enough to balance the increase in Seebeck's coefficient by the carrier scattering of Cu–Te/Cu₂SnSe₃ composites. The maximum α was $\sim 80 \mu\text{V}/\text{K}$ for the 1.2 vol.% Cu–Te/Cu₂SnSe₃ composite at 700 K. Figure 8 shows the temperature dependence of the power factor (PF) for all Cu–Te/Cu₂SnSe₃ samples. The 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite showed the best PF, and the maximum PF reached $6.3 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 700 K, which was ~ 1.4 times that of the Cu₂SnSe₃ matrix.

Figure 7. Temperature dependence of Seebeck's coefficient (α) of Cu–Te/Cu₂SnSe₃ composites.

Figure 8. Temperature dependence of the power factor (PF) of Cu-Te/Cu₂SnSe₃ composites.

3.3. Thermal Transport Properties

Figure 9 shows the temperature dependence of total thermal conductivity κ and lattice thermal conductivity κ_L for Cu-Te/Cu₂SnSe₃ composites. It can be seen that the addition of melt-spun Cu-Te decreased the κ and κ_L of Cu₂SnSe₃ thermoelectric material evidently. It is already reported that the micro-voids/nanopores or holey structures can suppress the average group velocities at low temperatures and this suppression is expected to intensify as the temperature increases. Therefore, the micro-voids/nanopores in Cu-Te/Cu₂SnSe₃ could potentially introduce additional phonon scattering and play a great role in reducing the κ_L by targeting long-wavelength phonon scattering. However, there was little difference in κ among the Cu-Te/Cu₂SnSe₃ composites in the whole temperature range. The κ is composed of κ_L and carrier thermal conductivity (κ_c). The κ_c can be estimated using the Wiedemann–Franz law, $\kappa_c = L\sigma T$, where L is the Lorenz constant and has a value of $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$ [20,21]. The κ_L can be calculated by subtracting the κ_c from κ . As the 0.8 vol.% Cu-Te/Cu₂SnSe₃ composite had a large κ_c , κ_L of the 0.8 vol.% Cu-Te/Cu₂SnSe₃ was minimal and $\sim 0.22\text{--}1.1 \text{ W/m}\cdot\text{K}$. The minimum κ_L of 0.8 vol.% Cu-Te/Cu₂SnSe₃ was $0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 700 K, which was 78% lower than that of the Cu₂SnSe₃ matrix. In addition, κ_L showed temperature dependence of T^{-1} in the whole temperature range, suggesting that phonon–phonon scattering dominated the scattering mechanism for the Cu-Te/Cu₂SnSe₃ composites.

Figure 9. The temperature dependence of thermal conductivity κ (a) and lattice thermal conductivity κ_L (b) for Cu-Te/Cu₂SnSe₃ composites.

3.4. Figure of Merit

Figure 10 depicts that temperature dependence of the dimensionless figure of merit (ZT) for Cu–Te/Cu₂SnSe₃ composites. ZT of all Cu–Te/Cu₂SnSe₃ composites increased with increasing temperatures. The addition of melt-spun Cu–Te improved the thermoelectric performance of Cu₂SnSe₃ thermoelectric material. The maximum ZT value of 0.45 was obtained at 700 K for the 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite, which was two times that of the Cu₂SnSe₃ matrix. Improvement in ZT of the Cu–Te/Cu₂SnSe₃ composite was mostly attributed to the decreased κ . The addition of melt spun Cu–Te had great effects on the microstructure and chemical composition of Cu₂SnSe₃ material. In addition, due to the presence of micro-voids/nanopores in the Cu–Te/Cu₂SnSe₃ composite, there might be another x value between 0.4 and 1.2 that give even better result. We will refine and optimize the x value in future work.

Figure 10. The dimensionless figure of merit of (ZT) of Cu–Te/Cu₂SnSe₃ composites.

4. Summary

The Cu–Te alloy ribbon containing nanocrystalline structures was prepared by melt spinning, and was composed of Cu_{2–x}Te, Cu₂Te, and Cu_{3–x}Te₂ phases. Both sides of Cu–Te ribbons had a uniform microstructure and the grain size was 400–800 nm. The Cu–Te/Cu₂SnSe₃ thermoelectric composites were prepared using the ball milling and spark plasma sintering method. The addition of melt-spun Cu–Te phases improved the thermoelectric performance of Cu₂SnSe₃ thermoelectric material. Increase in ZT of the Cu–Te/Cu₂SnSe₃ composite was mostly attributed to the decreased thermal conductivity. Maximum ZT of the 0.8 vol.% Cu–Te/Cu₂SnSe₃ composite was 0.45 at 700 K.

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