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Synthesis of bulk nanocrystalline Pb–Sn–Te alloy under high pressure

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Abstract

Pb–Sn–Te bulk nanocrystalline (NC) materials are prepared successfully by quenching melts under high pressure. The mean particle size is about 100 nm and the crystal structure is NaCl type. The mechanism of formation of the bulk NC alloy is explained: there is an increasing of the nucleation rate and a decrease in the growth rate of nuclei with increase of pressure during the solidification processes. The thermoelectric properties of Pb–Sn–Te bulk NC alloy are enhanced. This method is promising for producing thermoelectric materials with improved high-energy conversion efficiency.

1. Introduction

Many properties of nanocrystalline (NC) samples are found to be completely different from, and often superior to, those of the conventional polycrystalline or amorphous solid [1]—for example, an increased strength/hardness, improved ductility/toughness, an enhanced diffusivity. Preparation of large bulk NC material with clean grain boundaries and less porosity is of great importance to theoretical studies and practical applications. Recently, many methods of producing bulk NC materials have been developed—for example, the consolidation of powders of nanometre scale [2, 3]. However, it has been demonstrated that there are micropores in the NC material and impurities in the grain boundaries. Obviously, these are not favourable for fundamental research and application of NC materials.

Pressure-quenched (PQ) samples, which have the following advantages: dense NC bulk, clean crystalline interfaces, more homogeneous crystalline grain sizes, etc, can solve these problems.

Recently, there has been expanding interest in thermoelectric materials [4–6]. The performance of thermoelectric materials can be evaluated by the figure of merit defined as $Z = \sigma S^2 / \kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the total thermal conductivity. There have many methods proposed for improving the thermoelectric properties of materials by decreasing the thermal conductivity and enhancing the thermoelectric power figure σS^2 [7].

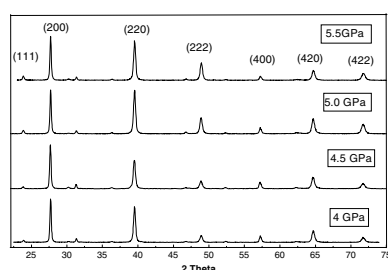


Figure 1. XRD spectra of Pb–Sn–Te alloy prepared at high pressure.

In many thermoelectric devices, for improving the high-energy conversion efficiency of the thermoelectric materials, forming FGM (functionally graded materials) is one of the most promising methods [8]. $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys with different x have usually been used as the segmented FGM for this purpose.

In this paper, a method of preparation of Pb–Sn–Te bulk NC materials by quenching melted Pb–Sn–Te powders within a certain pressure range at a given cooling rate is presented. The formation mechanism and thermoelectric properties of the bulk NC alloys are discussed.

2. Experimental procedure

Preparation of Pb–Sn–Te alloys was carried out using a cubic anvil high-pressure apparatus with a sample chamber of 23 mm.

The pressure was given by a calibration curve, which was established by determining the applied loads corresponding to the phase transformation pressure of bismuth, thallium, and barium. The cooling rate was given by measuring the variation of the thermal potential of chromel–alumel with time.

Phase analysis and grain size measurement for the PQ sample were performed by means of x-ray diffraction (XRD) and scanning electron microscopy (SEM). The resistivity was measured through a four-probe method at room temperature. The Seebeck coefficient was measured under Ar protection by a home-built apparatus. The temperature gradient was generated by a small resistive heater pasted on one edge of the sample, and was monitored by a copper–constantan thermocouple.

3. Results and discussion

3.1. Structure and phase analysis

Figure 1 shows the XRD spectra of the Pb–Sn–Te alloy prepared by quenching the melted Pb–Sn–Te at a cooling rate of 200 K s^{-1} at different pressures. By analysis of the XRD data and verification by SEM, it was concluded that the PQ samples are composed of NaCl-type structure with grain size less than 100 nm.

The SEM image of the PQ samples synthesized at high pressure and high temperature is shown in figure 2. From this image we can see that the grain sizes of PQ samples under the same pressure are homogeneous. This result indicates that the PQ method can not only synthesize bulk NC materials, but also homogeneously distribute the grain sizes. The same grain size induced symmetric properties in thermoelectric materials, which is discussed next.

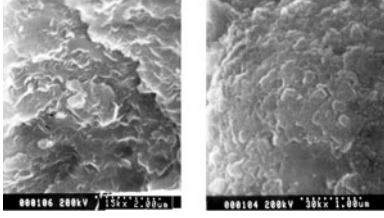


Figure 2. The SEM image of the Pb–Sn–Te alloy synthesized at high pressure.

3.2. Effect of pressure on the grain size

The mechanism of formation of the bulk NC materials and the influence of high pressure on its grain size were explained by the classical theory of homogeneous nucleation. The nucleation rate (I) and the growth rate (U) can be expressed as [9]

$$I = \exp\left[\frac{\alpha\sigma^3 V_s (T_m - T)^2 T}{RH_m^2 T_m^3}\right] \exp[-\Delta G^I/RT] \quad (1)$$

$$U = \{1 - \exp[-H_m(T_m - T)/RT]\} \exp[-\Delta G^{II}/RT] \quad (2)$$

where α is a geometrical constant, σ is the interfacial tension, H_m is the latent heat of crystallization, T_m is the crystallization of temperature, ΔG^I , ΔG^{II} are the activation energies for nucleation and crystal growth respectively, R is the universal gas constant, and V_s is the volume of solid per mole. Here, the change of σ with pressure can be neglected since σ is only weakly linked with pressure.

The mean grain size d is expressed in terms of U and I : $d = (U/I)^{(1/4)}$ [9]. It can be seen that the influence of pressure on the mean grain size d is dependent on the nucleation rate and growth rate.

From equation (1), the influence of pressure on the nucleation I can be expressed in the form

$$\frac{I(P)}{I(P_0)} = \exp\{[\Delta G^I(P_0) - \Delta G^I(P)]/RT\} \quad (3)$$

where P is pressure and $P > P_0$. In most alloy systems the relationship $\Delta G^I(P) < \Delta G^I(P_0)$ holds, which results in the nucleation rate during solidification increasing with increase of pressure. This indicates that there would be more nuclei and less space for the growth of the nuclei during solidification with pressure involved than in conventional solidification. Therefore, applying pressure during the solidification process is beneficial as regards obtaining fine crystalline grains, from the standpoint of nucleation.

The growing rate U depending on pressure is written as

$$U(P)/U(P_0) = \exp\{[\Delta G^{II}(P_0) - \Delta G^{II}(P)]/RT\}. \quad (4)$$

The activation energy for crystal growth $\Delta G^{II}(P)$ mainly depends on the diffusion activation energy. For most alloy systems, pressure makes the diffusion activation energy increase which makes the activation energy of the crystal growth increase. Because atomic diffusion is necessary for growth of nuclei, application of pressure in the solidification process makes the growth of crystalline nuclei more difficult. However, pressure is also helpful for producing fine crystalline grains, because it hinders the growth of nuclei.

The following expression gives the influence of pressure on the grain size d :

$$\frac{d(P)}{d(P_0)} = \exp\left\{\frac{[\Delta G^{II}(P_0) - \Delta G^{II}(P)][\Delta G^I(P) - \Delta G^I(P_0)]}{RT}\right\}. \quad (5)$$

Table 1. Thermoelectric properties of Pb_{0.8}Sn_{0.2}Te bulk nanometre-scale alloys measured at room temperature.

Pressure (GPa)	Resistivity (10 ⁻⁶ Ω m)	Seebeck coefficient (μV K ⁻¹)	Thermoelectric power figure (10 ⁻⁶ W m ⁻¹ K ⁻¹)
4.0	5.1	94.9	1765
4.5	4.3	89.6	1867
5.0	3.0	79	2080
5.5	2.5	72.5	2102

In conclusion, pressure can accelerate nucleation and restrain growth of nuclei during solidification, so application of pressure in the solidification process can make the crystalline grains fine, and makes it possible to obtain ingots with nanometre-sized crystalline grains, which agrees well with the experimental results.

3.3. Thermoelectric properties

The thermoelectric properties of Pb–Sn–Te prepared by PQ are listed in table 1 and are superior to the results in [8]. From this table, it can be seen that both the resistivity and the Seebeck coefficient decrease with synthesis pressure increase. The increasing of the carrier concentration under pressure may cause these results to be in good agreement with the results in [10, 11]. Due to the many advantages of high density, clean crystalline interfaces, and the homogeneous grain size in the PQ samples in comparison with other polycrystalline or NC materials, the resistivity did not go up with the grain size decrease. The Seebeck coefficient's slight reduction with the increase of pressure is caused by the change in energy gap structure under pressure, which is in good agreement with the results in [12].

The thermal conductivity is the sum of the contributions arising from the lattice thermal conductivity (phonon), K_l , and the electronic thermal conductivity, K_e ; i.e. $K = K_l + K_e$. In semiconductors, thermal conductivity is mainly caused by phonons; i.e. $K_l \gg K_e$ at low temperature. Compared with polycrystalline materials, PQ samples have more grain boundaries scattering phonons, which leads to reduction of the lattice thermal conductivity.

From the above analyses, it can be concluded that the figure of merit Z increases with σS^2 increase and thermal conductivity decrease. These results indicate that the PQ method is an effective method for synthesizing materials with improved properties.

4. Summary

Pb–Sn–Te bulk NC alloys were obtained by PQ melting mixed powders under high pressure, which is explained in terms of acceleration of nucleation and the restraining of growth of nuclei during solidification under high pressure. XRD results show that the main phase of the PQ samples is a NaCl-type structure.

The thermoelectric properties of Pb–Sn–Te prepared by the PQ method were improved.

This method is effective for synthesizing thermoelectric materials with enhanced efficiency.

Acknowledgments

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