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Experimental investigation and thermodynamic modeling of the Se–Sn–Te system

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ABSTRACT

Vertical section at the SnSe–Te joint in the Se–Sn–Te system was investigated using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) and differential thermal analysis (DTA). Combined with the present experimental results and experimental information of vertical sections, isothermal sections and liquidus projection in literature, the phase diagram and the thermodynamic property of the Se–Sn–Te system were modeled using the CALPHAD (CALculation of PHAse Diagrams) technique. The liquid was described as (Se, Sn, Te, SnSe, SnTe) through an associate model. The terminal solid solution phases of Se and Te were treated as hex (Se, Te), and Sn as bct (Sn). The intermetallic compounds, α/βSnSe and $SnSe_2$, were treated as $(Sn, Te)_{0.5}(Se, Te)_{0.5}$ and $(Sn, Te)_{0.3333}(Se, Te)_{0.6667}$, respectively, on the basis of the thermodynamic model in the Se–Sn binary system in literature and experimental solid solubility of Te in these compounds in Se–Sn–Te system. The compound SnTe was modeled as $(Sn, Se)_{0.5}(Se, Te)_{0.5}$ according to thermodynamic model in the binary Se–Te system and experimental solid solubility of Se in the Se–Sn–Te system. A set of self-consistent thermodynamic parameters of individual phases was obtained.

1. Introduction

It is well known that IV–VI-based compounds including Se, Sn and Te can be used as infrared optics, infrared spectrum detection [1] and excellent thermoelectric converters [2]. Se–Sn–Te films materials have also good characteristics for reversible optical recording. Each element in the ternary system has different functions. The selenium has a low thermal conductivity, which makes the film resistive to oxidation and ensures that the alloy of Se and Sn can have a high stability of the amorphous state both at room temperature and at a high-speed erasing, and most selenium based materials are preferred because of its commercial application [3,4]. The tellurium in an amorphous crystalline phase in the Se–Sn–Te film absorbs laser beams and has a low thermal conductivity when compared with other light-absorbing elements [4]. The tin is useful to obtain stable glassy alloys when added into the Se–Te binary alloy [5,6] and to enhance the transformation from the hexagonal phase (Se and Te) to the superconducting tetragonal phase during the sintering process of $FeSe_{0.5}Te_{0.5}$ samples [7]. Additionally, the thermoelectric effect of SnSe crystals enables a direct and reversible conversion between thermal and electrical energy, and provides a viable route for power generation from waste heat. SnSe crystals have the advantage of ultralow thermal conductivity and high thermoelectric figure of merit and enhance the efficiency of thermoelectric materials [8]. Moreover, the alloy in the two-phase of SnSe/SnTe system has a lower thermal conductivity and a better thermoelectric performance than that in one-phase Te [9]. In order to better understand the effect of Te on the microstructure and properties of Se–Sn based alloys, the knowledge of phase equilibrium in the Se–Sn–Te system is a prerequisite. Based on the study of the phase diagram, the solid solubility of Te in the Se–Sn alloys and the phase relation among each phase can be confirmed.

In the present study, the vertical section at the SnSe–Te joint in the Se–Sn–Te system was studied by XRD, SEM–EDS and DTA measurements [10–12], and the Se–Sn–Te system was optimized using the CALPHAD technique [13]. According to the calculated results, a boundary point should exist between the liquidus surfaces of αSnSe and βSnSe at the SnSe–Te joint. The aim of our experiments was to separate the liquidus surface of αSnSe and βSnSe. However, the crystal structure of two phases was too similar to be discriminated by means of the XRD results. The microstructures of samples were used to determine the primary phase in the liquidus surface projection, and DTA measurements were used to confirm the phase transformation temperature below 550 °C. The calculated results

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were compared with the present experimental results and experimental data from Refs. [14–16].

2. Experimental procedures

All samples with total mass of about 5 g were prepared from Se, Sn and Te of 99.99% purity in a muffle furnace with swing function (cinite SG1200). Before melting, the samples were weighted and sealed with quartz glass tubes. After the constituent elements had been completely mixed and melted, the sample tube was removed from the furnace and quenched in air.

The samples were cut into two halves using wire-electrode. One half was used for determining crystal structure by XRD [10] and microstructure by SEM [11]. The XRD was used to identify the crystal structure of the constituent phases. The XRD measurement was carried out on a Rigaku rotatory anode harrow X-pert diffractometer using Cu Kα radiation at 40.0 kV and 150 mA. The data was collected in the range of 2θ from 20° to 100° with a step size of 0.02°. The other half was ground into powders for determining phase transition temperatures by DTA [12], which was performed on a SDT Q600 (TA instruments). Alumina crucibles were used and measurements were performed under flowing argon atmosphere. Samples were investigated at a heating rate of 10 °C/min. The sample mass and heating rates were determined by the analysis of one sample at different testing conditions. An empty alumina crucible was used as the reference. The overall uncertainty of the determined phase transformation temperatures was estimated to be ±1 °C. In order to minimize the error, the instrument was calibrated before the experiment, the samples were ground into powders and the heating rate was as slow as 10 °C/min. The experimental alloy compositions were listed in Table 1. The SEM, XRD and DTA results of partial alloy samples were shown in Figs. 1–4, and the analysis of results was introduced in Section 5.1.

Table 1
Alloy compositions of ternary Se–Sn–Te alloys.

No.	Alloy composition (at.%)		
	Sn	Se	Te
#1	5	5	90
#2	6	6	88
#3	8	8	84
#4	10	10	80
#5	12	12	76
#6	14	14	72
#7	20	20	60
#8	30	30	40
#9	37	37	26
#10	45	45	10

3. Literature information

3.1. Se–Sn system

Pelabon and Moissan [17] first determined the liquidus of the Se–Sn system. Then the Se–Sn phase diagram was investigated by many researchers [18–22]. These data are in reasonable agreement between them. Later on, Baldé et al. [23] and Yamaguchi et al. [24] reported a small latent heat in SnSe, and determined the polymorphic transformation between αSnSe and βSnSe. Feutelais et al. [25] re-investigated the Se–Sn phase diagram by DSC and XRD measurements, in which liquid, two solid solutions, bct(Sn) and

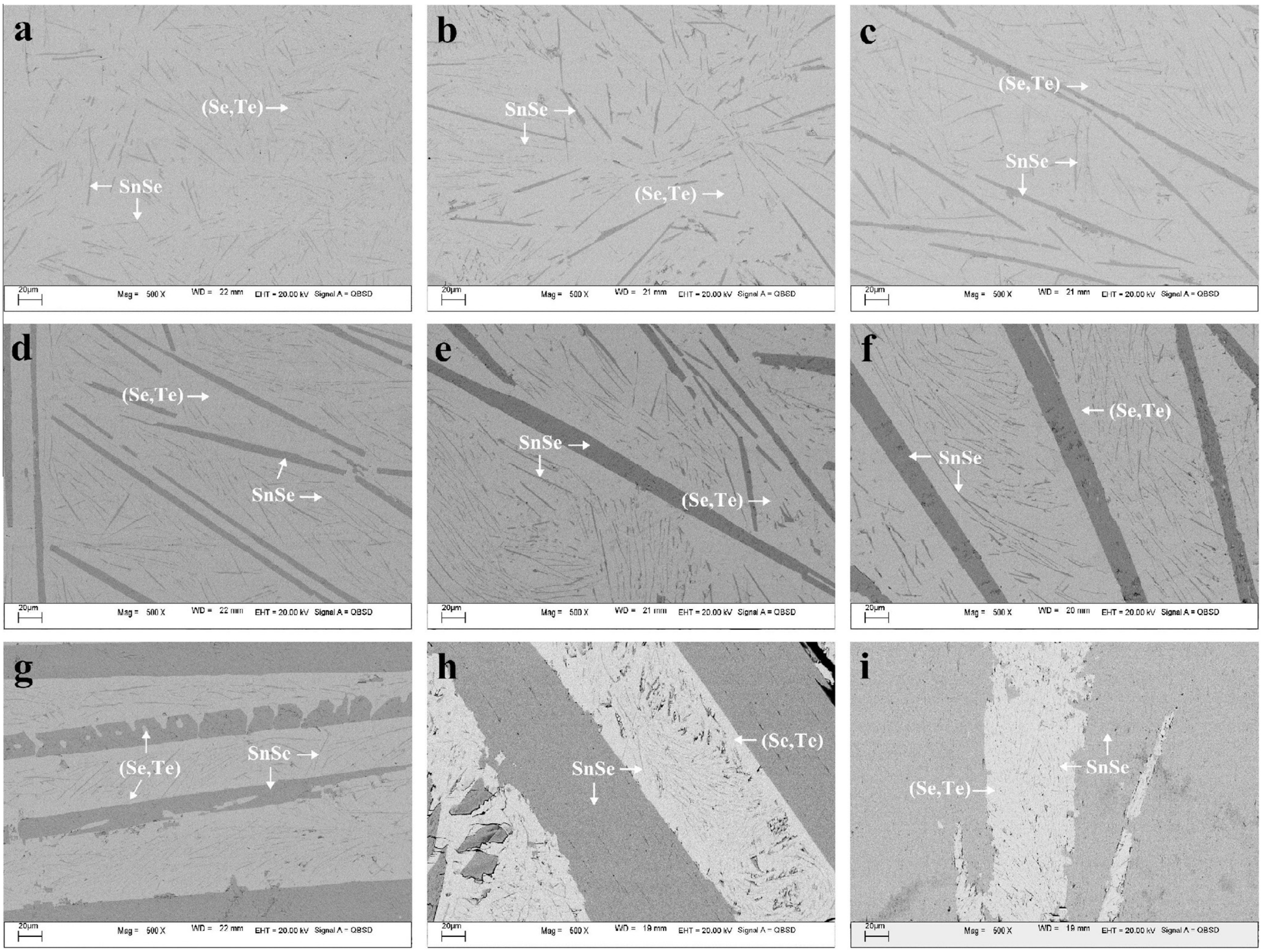

Fig. 1. BEI micrograph of alloy. (a) alloy #1, (b) alloy #2, (c) alloy #3, (d) alloy #4, (e) alloy #5, (f) alloy #6, (g) alloy #7, (h) alloy #9, and (i) alloy #10.