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Experimental reinvestigation and thermodynamic description of Bi-Te binary system

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ABSTRACT

The Bi-Te phase diagram was determined by equilibrium alloy method, combined with electron probe microanalysis (EPMA), X-ray diffraction (XRD) and thermal analysis (DSC). The experimental result shows that there is a β-phase with a large composition range at low temperature, while Bi_2Te and Bi_4Te_3 are relatively stable in the solid-liquid region. A consistent phase diagram that covers the experimental findings has been achieved. Based on the new experimental phase diagram, coupling with the reported thermodynamic data, the thermodynamic optimization of the Bi-Te binary system was carried out with the help of CALPHAD approach. A group of reasonable thermodynamic parameters was obtained.

1. Introduction

With the emergence of the energy crisis, research and development of applicable thermoelectric materials for waste heat recovery and power generation have drawn increasing interest in the past decade [1–4]. Among the most suitable materials, the Bi-Te alloys are well-known commercial materials for good thermoelectric properties at room temperature. However, the low ZT is still limiting its wide applications. Numerous efforts have been made to improve their thermoelectric performance [5–8]. The performance of Bi-Te alloys is strongly associated with the crystallographic structure, thermodynamic stability and phase transformation of Bi-Te compounds which can be readily extracted from the phase diagram and thermodynamic database of Bi-Te system [9–11]. Thus, the construction of reliable phase diagram and the understanding of phase transformation in Bi-Te alloys are of importance to tune the chemical composition and phase constitution of Bi-Te alloys, so as to advance the exploration of novel thermoelectric materials.

Although phase relations of Bi-Te system have been studied experimentally for several times, however, a phase diagram which can cover all available experimental results compatibly has not been achieved yet. The contradictions were concentrated on the identification of stable intermetallic compounds and the types and temperatures of relevant invariant reactions.

Hansen's early work [12] described the Bi-Te phase diagram into the combination of two simple eutectic reactions separated by a ridge like solid-solution phase (then dominated as β phase by Brown and Lewis [13]) in the central part. Accordingly, the β phase can be introduced by both eutectic reactions of L→Bi + β and L→Te + β at 266 °C and 413 °C, respectively. The detected invariant temperatures were then verified and agreed by other researchers [14,15]. Hansen's work was consolidated by Brown and Lewis [13], as shown in Fig. 1(a). Based on the evidence of X-ray diffraction, they measured the solidus of β, which indicated the β phase exhibited a broad solid solubility from 32 to 60 at % Te. The minerals Hedleyite (Bi_7Te_3), Wehrlite (BiTe) and Tellurbismuth (Bi_2Te_3) were suggested to be described into the single solid-solution β phase due to their close structural similarity as well as the progressive changes in the cell dimensions with change of composition [13]. However, the single β phase description hardly convinced the crystallgraphic scientists especially Glatz [14], and he employed both DTA and metallography to corroborate X-ray measurements in the region of β. It was conducted that congruent melting Bi_2Te_3 is stable as a single phase over a very narrow composition range and is separated from a bismuth-rich peritectic β-phase by a narrow two-phase field. Noticeably, a peritectic reaction L + Bi_2Te_3→β at 562 °C was identified and several enthalpic effects were detected [14]. From then on, thermal analysis was widely applied to determine the thermodynamic stability of compounds with specific stoichiometric ratios. The measured DTA readings were correlated with a series of peritectic reactions to form different compounds, which gave rise to an updated phase diagram compiled by Glazov et al. [16]. As shown in Fig. 1(b), four stable compounds, namely Bi_7Te_3, Bi_2Te, BiTe, and Bi_2Te_3 were present in Glazov's phase diagram. The degenerated solidus of stoichiometric Bi_2Te_3 and Bi_7Te_3 as well as the convex solidus of Bi_2Te and BiTe ,

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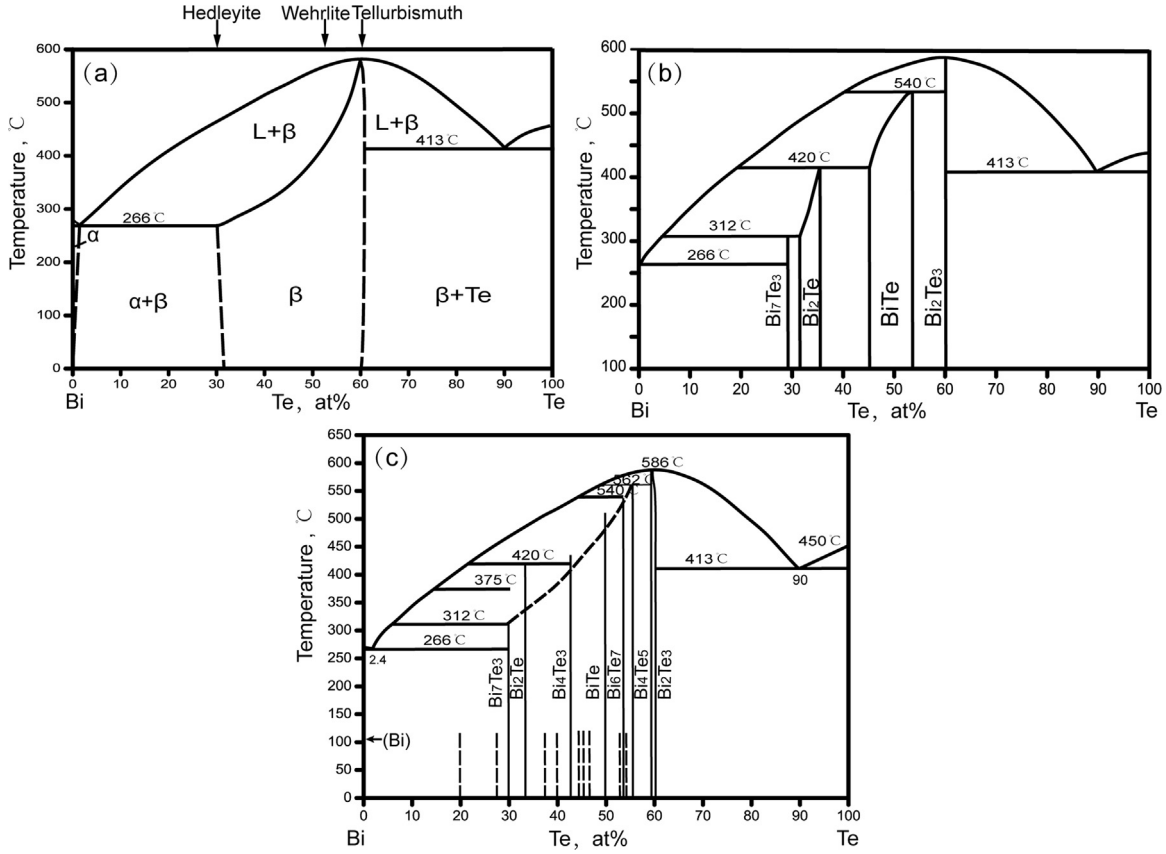

Fig. 1. Bi-Te phase diagram assessed by (a) Brown and Lewis [13], (b) Glazov et al. [16], (c) Okamoto and Tanner [17].

which have a homogeneous range, deviated from the smooth solidus in the region from 27 to 60 at% Te in the phase diagram depicted by Brown [13]. In the latest phase diagram compiled by Okamoto and Tanner [17], as shown in Fig. 1(c), more newly-synthesized compounds were included, so that the smooth solidus in Brown's phase diagram was approximately substituted by a succession of peritectic steps. However, the one-to-one mapping between peritectic temperatures and formed stoichiometric compounds had not been clarified. The tie-lines between solid phases and liquid phase were far beyond clearly outlined. Therefore, the Okamoto's compilation was indeed a compromised result. Due to the undetermined phase diagram of Bi-Te system and complicated structure-composition-energetic relationship of relevant intermetallic compound, we revised the Bi-Te phase diagram.

2. Experimental details

The Bi-Te binary phase diagram was studied by discerning the phase constitution and microstructure evolution of key alloy samples with different compositions. The nominal compositions of alloy samples #1-#12 are given in Table 1. The alloys were prepared from high purity Bi (99.99 wt%) pieces and pulverized Te (99.99 wt%). The weighed raw materials were sealed in quartz tubes under the protection of inert argon gas and then melted at 700 °C for 2 h followed by water quench. The as-cast samples were subjected to microstructure observation and phase composition analysis. According to former experiment of Bi-Te system [14], the composition of same sample will change after annealed due to the volatility of Tellurium. We thus determined the compositions of each sample before and after annealing by chemical analysis. The compositions of as-cast samples barely deviate from the nominal ones shown in Table 1, while after annealed, about 1–2 at% tellurium lost. In order to conduct a phase diagram more precisely, actual compositions were taken into consideration for annealed sample analysis.

The as-cast samples were sealed in evacuated quartz tubes again and annealed below the solidus, appropriate temperatures are applied for different alloys to achieve equilibrium more completely (see Table 1). After long-term annealing, the alloys were quenched into ice water to preserve the high-temperature microstructure. The microstructure was observed by scanning electron microscopy(SEM) (FEI Quanta 250). Chemical composition of phases was detected by electron probe microanalysis (EPMA) (JXA-8800R, JEOL, Japan) equipped with OXFORD INCA 500 wave dispersive X-ray spectrometer(WDS). X-ray Powder Diffraction (XRD) was employed to identify the phase constitution of samples. It was performed on a Rigaku D-max/2550VB + X-ray diffractometer using a Cu Ka radiation. Differential Scanning Calorimetry & Thermo-Gravimetric Analysis(DSC/TGA) was adopted to determine the invariant temperatures in alloys. It was carried out on Netzsch 449C under Ar-atmosphere with a heating rate of 10 K/min. In consideration of the volatility of Tellurium, each sample was put into the alumina cup with a lid.

3. Experimental results and analysis

3.1. As-cast microstructure

Fig. 2(a)-(f) illustrate the as-cast microstructure of alloys #3-#8, respectively. The dark phase shows a lenticular shape and distributes randomly, indicating it is the primary phase. The light phase serves as a matrix, which solidified from the residual liquid. The EPMA to the central part of the primary laths determined different compositions in individual samples. Increased with alloy composition, the Te content at the central lath also shows an increasing tendency. More importantly, there is inhomogeneous composition distribution of primary laths in individual samples. The EPMA detected decreasing composition profiles of Te from the inner part to the boundary for the cross-section of the primary laths. Taking alloy #4 as an example (Fig. 2(b)), the content of Te was detected as 47 at% in the central part of the lath and gradually