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Phase equilibria in the Ge-Mn-Ti ternary system at 973 K, 1073 K and 1173 K

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ABSTRACT

Phase relationships in the Ge-Mn-Ti ternary system have been studied through alloy samples approach. Assisted with Electron Probe Microanalysis (EPMA) and X-ray diffraction (XRD) techniques, isothermal sections at 973 K, 1073 K and 1173 K of this system were constructed and existence of 2 ternary phases, i.e. GeMnTi and Ge_2MnTi, were confirmed. In addition, remarkable ternary solubilities in some binary compounds were detected, e.g. Ge in Mn_2Ti and Mn in Ge_5Ti_6 can be up to 15 at% and 50 at% at 1173 K, respectively. Furthermore, the substitution of Ti by Mn atoms in Ge_5Ti_6 was confirmed with Rietveld refinement results of solid solutions, $Ge_5(Mn_{0.30}Ti_{0.70})_6$ and $Ge_5(Mn_{0.67}Ti_{0.33})_6$.

1. Introduction

Hydrogen is an environmentally friendly energy which has promising prospect for future energy sources, but its storage still remains a challenge [1]. Among those numerous storage methods, metal hydrides are very effective and safe for storing large amounts of hydrogen [2–4]. Mn-Ti based alloys with Laves phase AB_2 structure are of technical and commercial interest, performing high hydrogen capacity, easy activation, good hydriding-dehydriding kinetics and excellent cycle property [5–7]. To improve the hydrogen storage properties of the Mn-Ti-based alloys, effects of other transition metals, such as Cr, Zr, V, Mo and W, have been investigated extensively [8–12]. Until now, the influence of Ge on the stability of Mn_2Ti based hydrogen storage material have not been reported.

The knowledge concerning phase relationships and transformations in the Ge-Mn-Ti system could be a guidance for subsequent study of novel hydrogen storage material. Information of binary Mn-Ti and Ge-Mn systems has been extensively investigated experimentally and through thermodynamic calculation. As for the Mn-Ti system, Murray [13] summarized a variety of experimental phase equilibria firstly, later optimized by Saunders et al. [14] and Chen et al. [15,16]. The assessments by Chen et al. [15,16] are well consistent with the reported experiments and thus are adopted in this work. Gokhale et al. [17] originally published the complete phase diagram of the Ge-Mn system, and the thermodynamic description was reported by Kanibolotskii et al. [18] later. Recently, a satisfactory thermodynamic assessment of the Ge-Mn system has been carried out by Berche et al. [19], mainly adopting the experimental data obtained by Wachtel et al. [20,21], Gupta et al. [22] and Zwicker et al. [23].

Dissimilar to the Mn-Ti and Ge-Mn binary systems, the phase diagram of Ge-Ti system is still controversial. In Massalski's compilation [24], the Ge-Ti binary system was evaluated mainly based on the experimental diagram of Rudometkina et al. [25]. Recently, Liu et al. [26] re-assessed this system and only concerned three stable intermediate phases, i.e. Ge_3Ti_5, Ge_5Ti_6 and Ge_2Ti. Nevertheless, the compound Ge_4Ti_5 was later reported as a new phase in the Ge-Ti system by Bittner et al. [27]. In addition, the $GeTi_3$ phase, formerly considered to be an unstable phase by Liu et al. [26] and Jain et al. [28], was recently confirmed to be a stable phase by Xie et al. [29].

Phase equilibria of the well accepted boundary binary systems, Mn-Ti [15], Ge-Mn [19] and Ge-Ti [27], are presented in Fig. 1.

So far, little information about phase relations in the Ge-Mn-Ti ternary system has been reported. To the best of our knowledge, only three ternary compounds, i.e. GeMnTi, Ge_2MnTi, $GeMnTi_2$ and their crystal structure [30] (see Table 1) along with partial phase relationships in the Mn-rich corner at 1173 K [31] were reported. The present work is an experimental study of phase relations in the Ge-Mn-Ti system at 973 K, 1073 K and 1173 K through alloy samples approach.

2. Experimental details

More than 50 samples have been prepared. Starting materials of high purity (Ge: 99.99%, Mn: 99.99%, Ti: 99.99%, China New Metal Materials Technology Co., Ltd.) were adopted to prepare the experimental alloys. The weight of each sample was limited to about 6 g. Pre-determined amount of each raw material was weighed by analytical balance, followed by arc-melting on a water-cooled copper plate under purified argon

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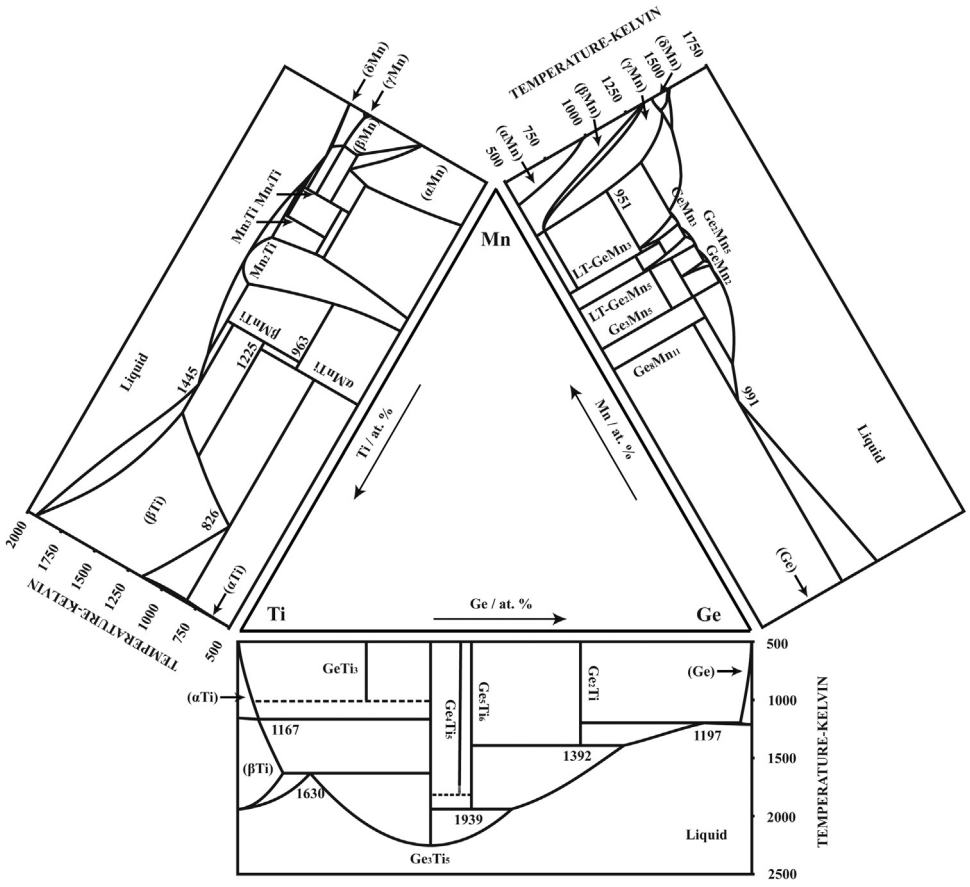

Fig. 1. Binary phase diagrams constituting the Ge-Mn-Ti ternary system [15,19,27].

atmosphere with titanium as getter material placed in the arc chamber. To ensure a good homogenization, all samples were turned over before each melting and re-melted at least 3 times. The weight losses of the so obtained as-cast button shaped alloys did not exceed 1%. Subsequently, majority of samples were sealed in evacuated quartz capsules and then heat-treated at 973 K for 90 days, 1073 K for 60 days and 1173 K for 40 days. After annealing, alloys were taken out quickly and quenched into water. These samples were ground on abrasive paper, polished with diamond paste and cleaned with alcohol in a standard method.

Constituent phases of samples were investigated by electron probe microanalysis (EPMA) (JXA-8800R, JEOL, Japan) equipped with OXFORD INCA 500 wavelength dispersive X-ray spectrometer (WDS). Standard deviations of the measured concentration are ± 0.6 at%. The total mass percent of Ge, Mn and Ti in each phase is in the range of 97–103%, so the effect of reactions between samples and silica capsules could be neglected. Different spots in each sample were examined by EPMA and the data corresponding to a same phase in one sample were averaged as the final phase composition. X-ray diffraction (XRD) was also performed to most of the samples using a Cu Kα radiation on a Rigaku D-max/2550 VB + X-ray diffractometer at 40 kV and 250 mA in continuous mode with a step size of 0.02° at a speed of 8°/min. High-quality powder XRD patterns of two samples within the Ge_5Ti_6 ternary solid solution, $Ge_5(Mn_{0.30}Ti_{0.70})_6$ and $Ge_5(Mn_{0.67}Ti_{0.33})_6$, were collected at room temperature using a Rigaku D-max/2550 VB + X-ray diffractometer (with Cu Kα radiation) in FT-mode. The scan (2θ) range was from 5° to 100° with a step size of 0.02° and a count time of 2 s per step.

3. Results

3.1. Phase equilibria at 973 K

Phase equilibria of the Ge-Mn-Ti ternary system at 973 K were studied covering almost entire composition range. All samples present a three-phase microstructure or two-phase microstructure and no more than three phases coexisted in annealed alloys, suggesting that a full equilibrium has been reached or nearly reached for the annealed Ge-Mn-Ti alloys at 973 K. The constituent phases in annealed alloys at 973 K are summarized in Table 2.

Fig. 2 illustrates the constituent phases in A3 alloy. As seen from Fig. 2a, dark (γMn), gray $GeMn_3$ and white GeMnTi coexist, implying this alloy locates in the three-phase area (γMn) + $GeMn_3$ + GeMnTi. This is confirmed by X-ray diffraction (Fig. 2b).

Microstructure of alloy A14 and A15 were respectively presented in Fig. 3a and b. With EPMA-WDS analysis, it is seen that alloy A14 consists of (αTi), (βTi) and $GeTi_3$, while alloy A15 consists of (βTi), $GeTi_3$ and Ge_3Ti_5, in agreement with its XRD pattern (Fig. 4a). So, it is concluded that these two alloys at 973 K locate in three phase region of (αTi) +(βTi) + $GeTi_3$ and (βTi) + $GeTi_3$ + Ge_3Ti_5, respectively. This indicates that phase $GeTi_3$ is stable at 973 K, similar to the case in the Ge-Ni-Ti system [29]. As a supplement, Fig. 4b represents the typical XRD pattern of alloy A16 turning out to be in a two-phase region (Ge) + Ge_2MnTi, and it is also confirmed by EPMA-WDS as listed in Table 2.

Based on experimental results, the isothermal section of the