Phase Diagram Investigations of the Bi-Ti System

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The liquidus and invariant reaction temperatures were measured by thermal analyses for Bi-Ti alloys containing 0-65 at.% of Ti. The liquidus temperatures were clearly much lower than the literature values. Equilibrium experiments showed the existence of a new phase, Bi_2Ti_3. However, the reported Bi_3Ti_2 phase was not observed in the present study. The temperatures of the peritectic reaction involving Bi_2Ti, Bi_9Ti_8, and Bi_2Ti_3 were also clarified to be 425, 930, and 970 °C, respectively. Thus, a new phase diagram of the Bi-Ti system was constructed.

1. Introduction

Many efforts to construct the phase diagram of the Bi-Ti system have been made by several researchers.[1-8] The Bi-Ti phase diagram was drawn by Murray in 1994,[1] but only two intermetallic compounds, $BiTi_2$ and $BiTi_3$, were known at that time along with their crystal structures.[2,3] This phase diagram was adopted by Massalski in 1996.[4] In 1997, Richter and Jeitschko[5] reported a new compound Bi_9Ti_8 as well as its crystal structure. Furthermore, in 2006, Vassilev[6] discovered new three phases, Bi_2Ti, Bi_3Ti_2, and BiTi by a solid/liquid diffusion couple method in quartz tubes at 400 to 700 °C, although the BiTi phase was considered to be identical with the previously reported Bi_9Ti_8. In 2010, considering all these reports, Okamoto[7] proposed the Bi-Ti phase diagram where Bi_9Ti_8 was chosen instead of BiTi. However, the liquidus and invariant reaction temperatures, particularly in the bismuth-rich region, were determined tentatively without detailed investigations. Only Weeks[8] studied the bismuth-rich region (less than 5 at.% of Ti) at 300 to 700 °C by annealing Bi in Ti crucibles or mixing Bi and Ti in Fe or Cr crucibles. No other work on the liquidus in the bismuth-rich region has been done.

In the present study, we determined the liquidus and invariant reaction temperatures of Bi-Ti alloys (0-65 at.% of Ti) by thermal analyses. Equilibrium experiments were also carried out to explore the intermetallic compounds and invariant reactions.

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2. Experimental

Bismuth (99.999%, supplied by Kamioka Mining & Smelting Co. Ltd.) and sponge titanium (>99%, Wako Pure Chemical Industries, Ltd.) were mixed with certain compositions as summarized with the results in Table 1. These mixtures in MgO crucibles were placed in a stainless steel container in a glove box filled with Ar gas and a lid was put on. The container was moved to atmosphere and sealed by TIG welding. In order to make homogeneous alloys, prethermal treatments were performed at 1000 °C (for the alloy containing 0-40 at.% of Ti) or 1200 °C (for the alloy containing 45-65 at.% of Ti). After 40 h, the alloys were quenched in water at room temperature. The alloys were heated again in a MgO crucible. The crucible was placed in another stainless steel container and a lid with a hole was welded. The thermocouple with a MgO protector tube was inserted through the hole to measure the temperatures in the alloys. Figure 1 shows a schematic illustration of the apparatus. The stainless steel containers were heated and held at 1000-1200 °C for over 3 h in an Inconel or alumina vessel filled with Ar gas. Then, the furnace was turned off and the temperature of the alloy was monitored during cooling. After cooling to room temperature, some alloys were used for heating curve measurements.

The Bi-Ti alloys containing 30, 40, 50, and 65 at.% of Ti in the MgO crucible in the closed stainless steel container were employed for equilibrium experiments, the conditions of which are summarized in Table 2. Except for Exp. #1, the mixtures of Bi and Ti were held at higher temperatures than their liquidus temperatures (established in this study) for 40 h to make homogeneous alloys in advance. Afterward, the stainless steel containers were cooled in the furnace to the holding temperatures as shown in Table 2. They were held for several tens of hours and then quenched in water.

The phases in the alloy were identified by an x-ray diffractometer (XRD, CuKα, X'pert Pro, PANalytical, Almelo). The compositions of Bi and Ti were determined by energy dispersive x-ray spectroscopy (EDX, EDAX VE-9800), using a scanning electron microscope (SEM, KEYENCE VE-7800), and inductively coupled plasma atomic emission spectrometry (ICP-AES, SII SPS3500). The EDX results were calibrated on the basis of the results by ICP analysis.

Table 1 Temperatures of the liquidus and invariant reactions of the Bi-Ti alloys determined by heating and cooling curve measurements

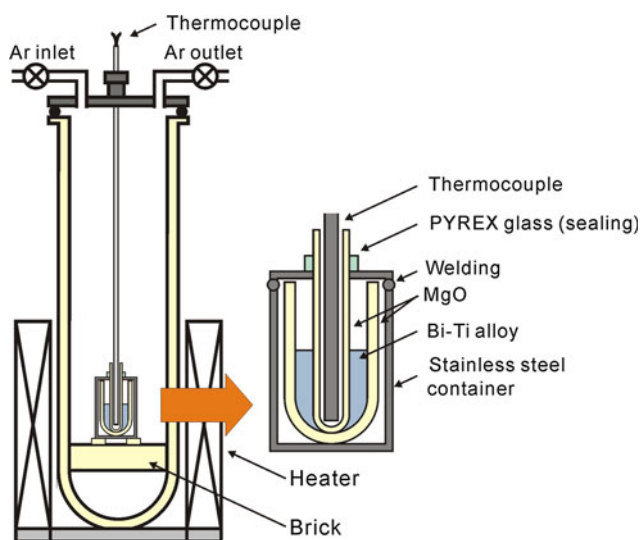| Bi:Ti, at.%	Cooling curve, °C				Heating curve, °C	
	Liquidus temp.	Invariant reaction I	Invariant reaction III	Invariant reaction IV	Invariant reaction I	Invariant reaction II
100:0	⋯	268	⋯	⋯	271	⋯
95:5	710	266	⋯	⋯	255	425
90:10	790	264	⋯	⋯	249	417
85:15	837	265	⋯	⋯	251	415
80:20	864	265	⋯	⋯	⋯	⋯
75:25	883	267	⋯	⋯	256	424
70:30	895	262	⋯	⋯	252	418
65:35	911	261	⋯	⋯	⋯	⋯
60:40	940	259	925	⋯	254	423
55:45	959	267	928	⋯	⋯	⋯
50:50	972	⋯	940	⋯	⋯	422
45:55	984	⋯	936	⋯	⋯	⋯
40:60	1053	⋯	⋯	967	⋯	⋯
35:65	1123	⋯	⋯	972	⋯	⋯

Fig. 1 Schematic illustration of the apparatus for cooling and heating curve measurements

3. Results and Discussion

3.1 Cooling and Heating Curve Measurements

Figure 2 shows the temperature and the time derivative of temperature (dT/dt) acquired by (a) cooling and (b) heating curve measurements of the alloy containing 40 at.% of Ti. Four perturbations on cooling and heating curves were observed. The onset temperatures of the perturbations were taken as the temperatures of the liquidus or invariant reactions. It is considered that the perturbation at 940 °C in the cooling curve measurement is related to the reaction at liquidus and others to the invariant reactions (I, II, and III). Figures 3 and 4 show the time derivative of temperature against temperature acquired by cooling and heating curve measurements of the alloys with other compositions, and the temperatures of liquidus and invariant reactions were determined as summarized in Table 1. Four types of invariant reactions (I-IV) were observed. The temperatures of liquidus and invariant reactions were plotted on the phase diagram reported by Okamoto in Fig. 5. In the figure, open symbols denote the results from the cooling curve and the closed symbols are the results from the heating curve. Determined temperatures of liquidus and invariant reaction are indicated by arrows. Most remarkable is that the liquidus temperatures are much lower than the reported values.[8] In addition, the temperatures of the invariant reactions II, III, and IV are significantly different from those in the previous phase diagram.

Reaction I is melting/solidification of Bi. The melting point of pure Bi was determined to be 268 °C, and this is in good agreement with the literature value (271 °C).[7] This result means that the measurements were done successfully. The reason why our value is a little lower than the reported melting temperature of pure Bi may be because a eutectic reaction occurs. However, we cannot declare whether it is eutectic or peritectic since it may include some errors caused by supercooling or thermal gradient in the alloy. It is deduced from the reported phase diagram that reactions II and III are associated with peritectic reactions. The invariant reaction II was observed only by the heating curve measurement. This would be because the heating rate (10 °C/min) was five times higher

Table 2 Experimental conditions of equilibrium experiments and the compositions of each phase determined by EDX point analyses

Exp.#	Bi:Ti, at.%	Homogenization		Holding		EDX result			
		Temp., °C	Time, h	Temp., °C	Time, h	Phase	Bi, at.%	Ti, at.%	Conceivable compounds
1	60:40	...	...	900	65	A	97.5	2.5	Liquid
						C	53.0	47.0	Bi_9Ti_8
						D	40.4	59.6	Bi_2Ti_3
						E	32.0	68.0	$BiTi_2$
						F	23.8	76.2	$BiTi_3$
						G	2.7	97.3	(Ti)
2	70:30	1000	40	420	45	A	96.9	3.1	Liquid
						B	65.2	34.8	Bi_2Ti
						C	51.5	48.5	Bi_9Ti_8
3	70:30	1000	40	430	45	A	95.8	4.2	Liquid
						C	52.4	47.6	Bi_9Ti_8
4	50:50	1150	40	850	265	C	54.9	45.1	Bi_9Ti_8
						D	43.9	56.1	Bi_2Ti_3
						E	35.0	65.0	$BiTi_2$
5	35:65	1200	40	950	95	D	39.3	60.7	Bi_2Ti_3
						E	32.4	67.6	$BiTi_2$
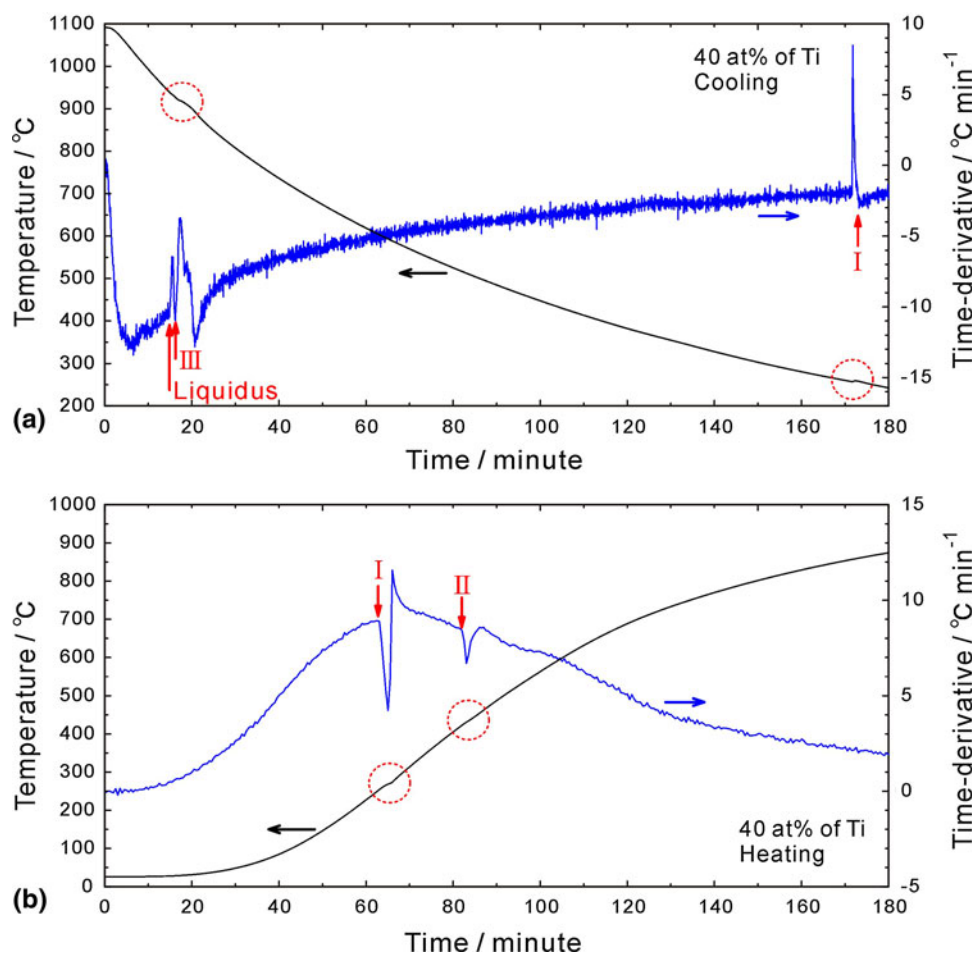
Fig. 2 Temperature and time derivative of temperature against time obtained by cooling curve measurements (a) and heating curve measurements (b) of the alloy containing 40 at.% of Ti. The arrows indicate the beginnings of rapid changes in time derivative caused by the reaction at liquidus and invariant reactions
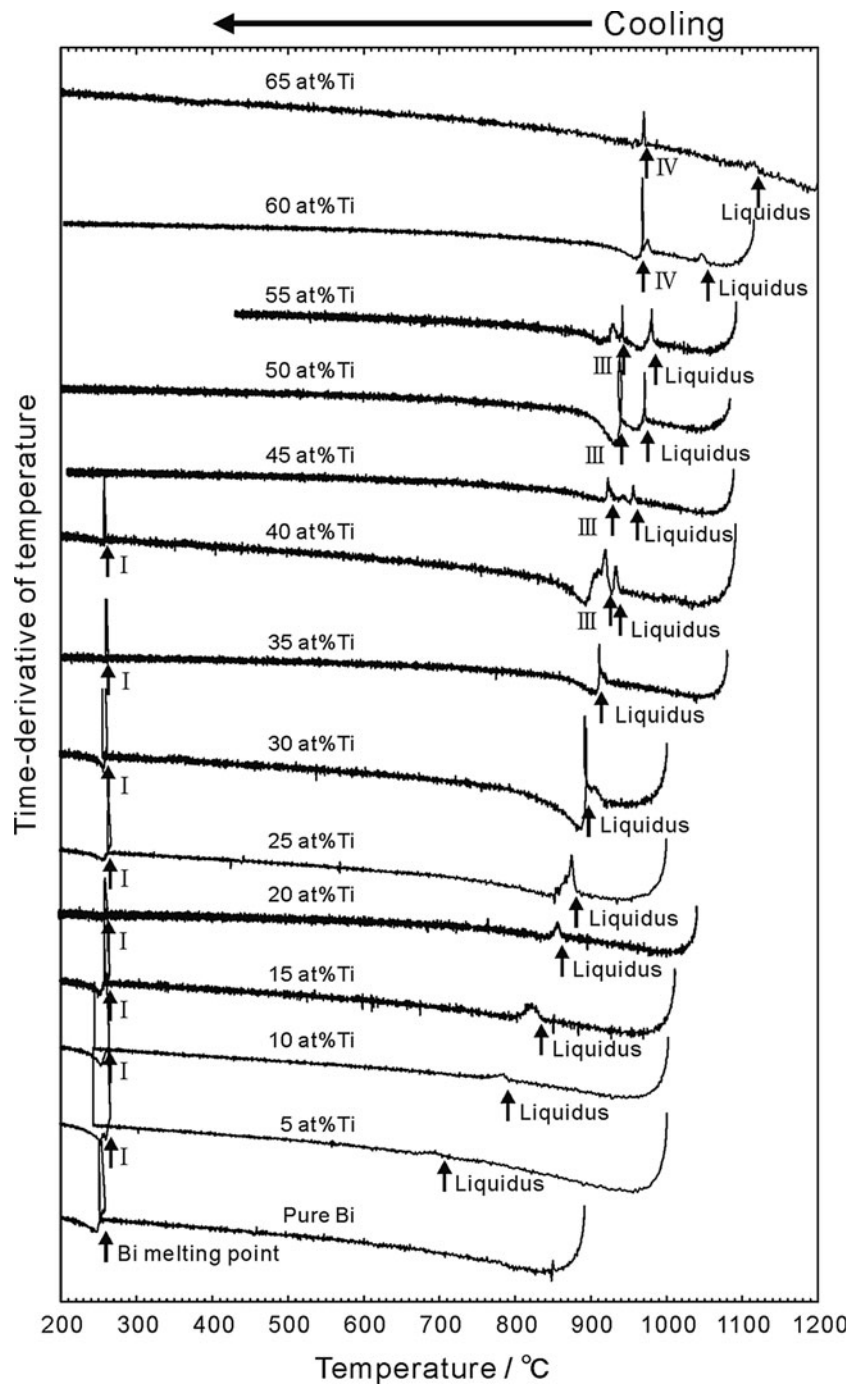
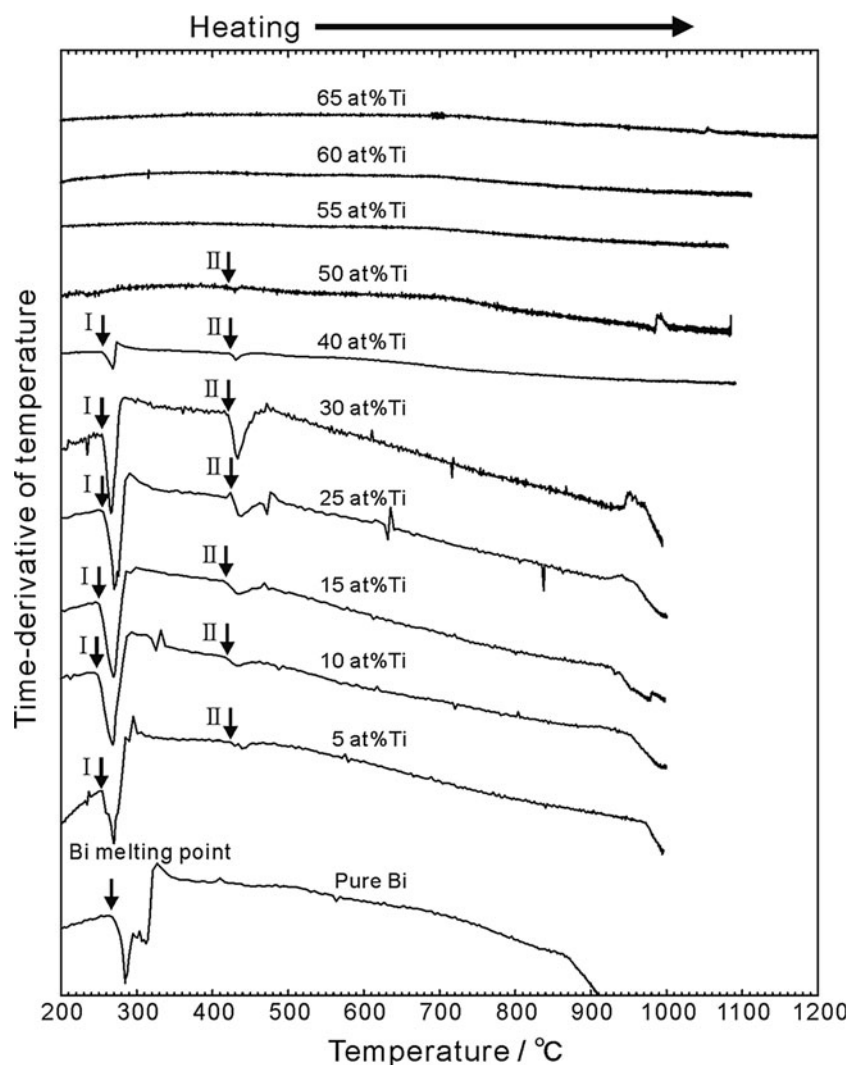**Fig. 3** Time derivative of temperature against temperature acquired by cooling curve measurements of the alloys containing 0-65 at.% of Ti. The measurement of the alloy containing 55 at.% of Ti was stopped at 400 °C

than the cooling rate (2 °C/min) at 500-400 °C. It is considered that the cooling rate was too low to get a clear break on the curve. On the other hand, reaction III and the reaction at liquidus were not observed by the heating curve measurement. This is ascribed to a small amount of the intermetallic compounds and the low heating rate (1 °C/min) above 900 °C.

3.2 Equilibrium Experiment

In order to identify the invariant reactions II, III, and IV, equilibrium experiments were performed. Figure 6 shows the SEM images of the alloy containing 40 at.% of Ti held at 900 °C for 65 h (Exp. #1). Seven different phases were observed and their compositions are shown in Table 2. The darkest phase (G) in Fig. 6 is Ti phase. It

Fig. 4 Time derivative of temperature against temperature acquired by heating curve measurements of the alloys containing 0-65 at.% of Ti

is considered that undissolved Ti remained since the diffusion of Ti and Bi in the solid intermetallic compounds is kinetically limited. Around the (G) phase, $BiTi_3$ (F), $BiTi_2$ (E), Bi_2Ti_3 (D), Bi_9Ti_8 (C), and liquid phase (A) were identified. Note that Bi_2Ti_3 is a new phase which has never been reported, and the reported Bi_3Ti_2 was not detected in this condition.

To make sure of the invariant reaction II, the alloys containing 30 at.% of Ti held at 420 and 430 °C for 45 h (Exp. #2, 3) were characterized by SEM-EDX (Fig. 7; Table 2) and XRD (Fig. 8). At 420 °C (Exp. #2), three phases, (A), (B), and (C), were observed. Phases (A) and (C) were the liquid phase and Bi_9Ti_8, respectively. Phase (B)

is probably Bi_2Ti by the EDX results. The XRD pattern of Bi_2Ti is not known, but some peaks corresponded to the pattern in the card of JCPDS #00-051-1006,[9] although there is no composition information about this card. At 430 °C (Exp. #3), on the other hand, only liquid (A) and Bi_9Ti_8 (C) phases were identified by EDX, although the XRD pattern showed a small peak at 31° due to Bi_2Ti. It is considered that a small amount of Bi_2Ti was precipitated when the alloy was cooled during quenching in water. These results suggest that invariant reaction II is
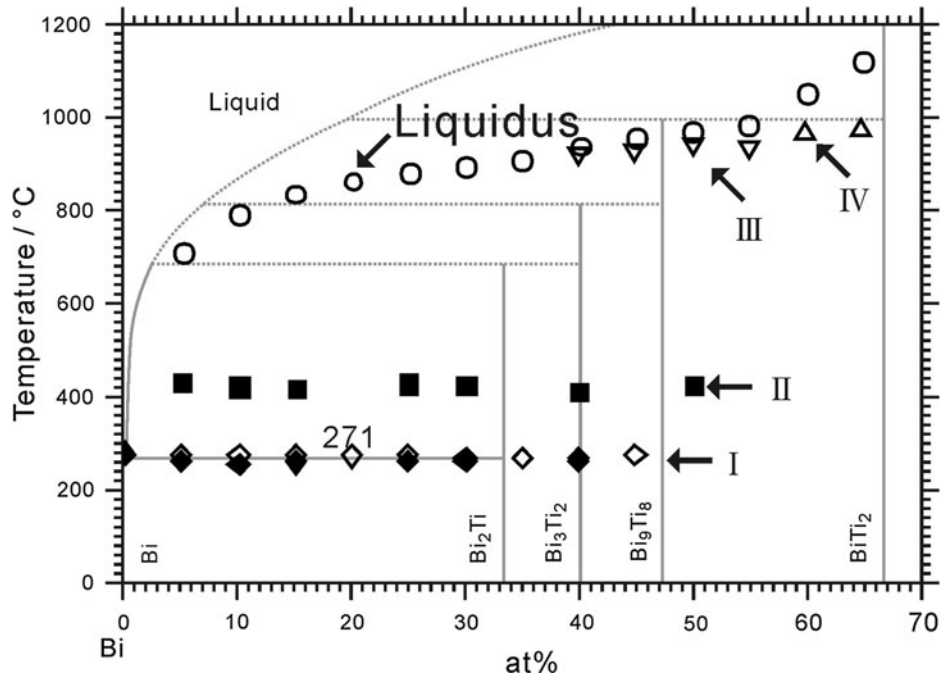
$$L + Bi_9Ti_8 = Bi_2Ti$$
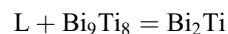
Fig. 5 Temperatures of the liquidus and invariant reactions obtained by cooling curves (blank) and heating curves (solid) on the reported phase diagram[7]
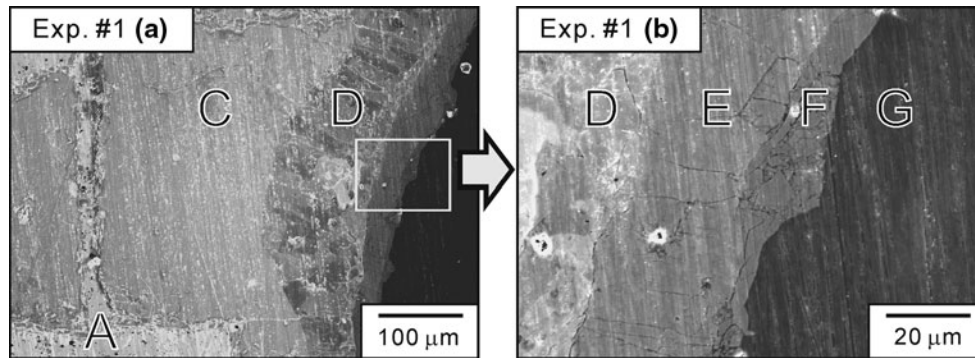

Fig. 6 SEM images of the alloy containing 40 at.% of Ti held at 900 °C for 65 h (Exp. #1). (b) is a high magnification image of the marked area in (a)
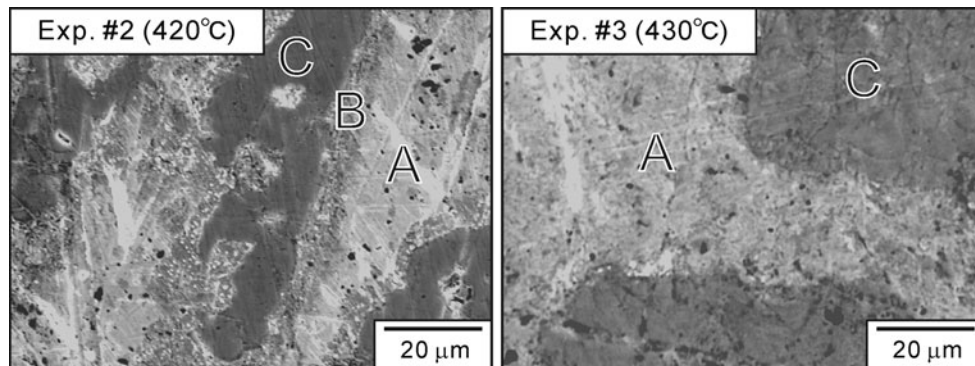

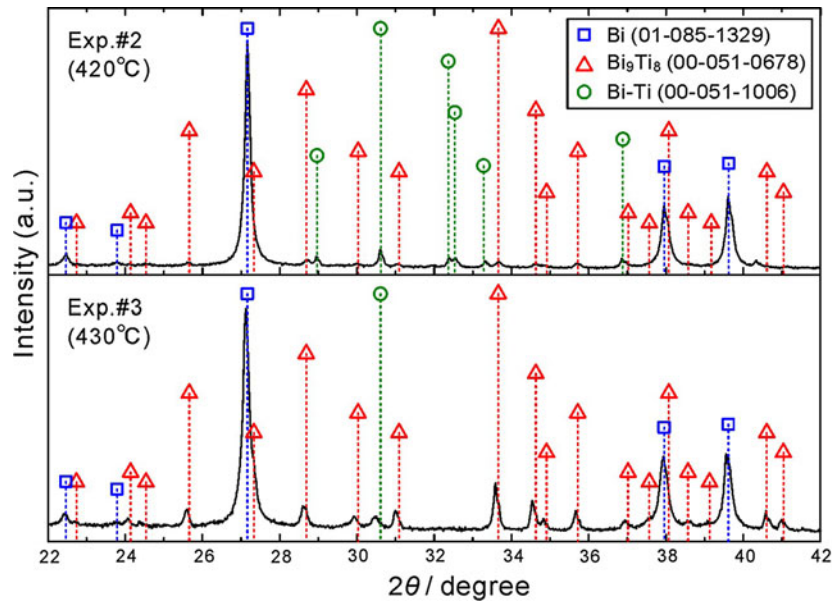**Fig. 7** SEM images of the alloys containing 30 at.% of Ti held for 45 h at 420 °C (Exp. #2) and at 430 °C (Exp. #3)

Fig. 8 XRD patterns of the alloys containing 30 at.% of Ti held for 45 h at 420 °C (Exp. #2) and at 430 °C (Exp. #3)
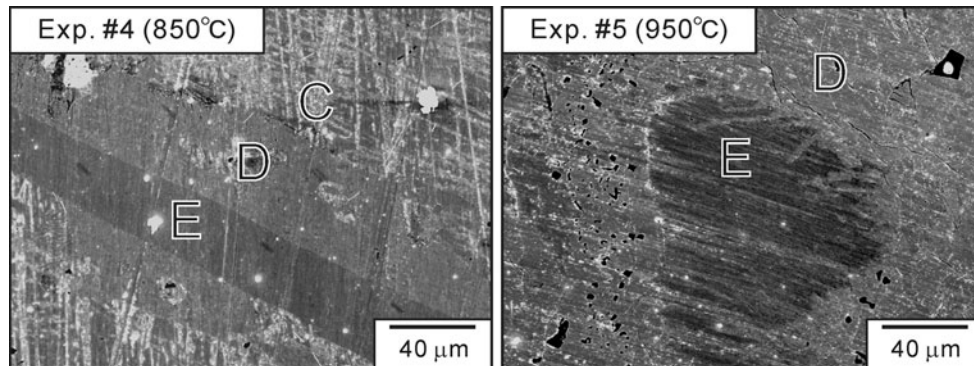

Fig. 9 SEM images of the alloys containing 50 at.% of Ti held at 850 °C for 265 h (Exp. #4) and 65 at.% of Ti held at 950 °C for 95 h (Exp. #5)

and its temperature is between 420 and 430 °C. Here, Bi_9Ti_8 remained in the alloy of Exp. #2 (420 °C) because of the slow formation of Bi_2Ti.

The SEM images of the alloys containing 50 and 65 at.% of Ti held at 850 and 950 °C (Exp. #4, 5) are shown in Fig. 9 and the results of EDX are given in Table 2. Bi_9Ti_8 (C), Bi_2Ti_3 (D), and $BiTi_2$ (E) were observed in Exp. #4. $BiTi_2$ remained because of the slow peritectic reaction ($L + BiTi_2 \rightarrow Bi_2Ti_3$). Considering this kinetic factor,

Bi_2Ti_3 and Bi_9Ti_8 are in equilibrium at 850 °C. The result of Exp. #5 indicates that Bi_2Ti_3 (D) and $BiTi_2$ (E) were in equilibrium at 950 °C. Thus, we conclude that invariant reaction III at 930 °C is

$$L + Bi_2Ti_3 = Bi_9Ti_8$$
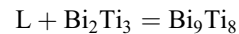
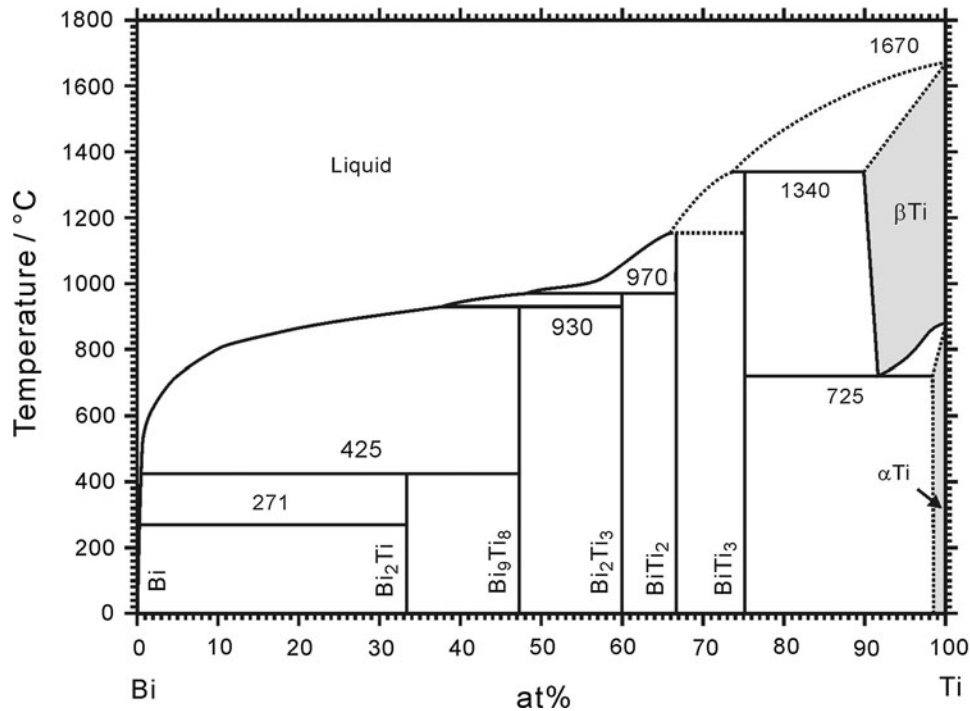and reaction IV at 970 °C is

$$L + BiTi_2 = Bi_2Ti_3.$$
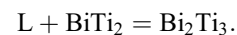
Fig. 10 The Bi-Ti phase diagram constructed by thermal analyses and equilibrium experiments

4. Conclusions

The Bi-Ti phase diagram was constructed by thermal analyses and equilibrium experiments as shown in Fig. 10. The liquidus temperature was significantly lower than the reported value. A new phase containing about 60 at.% of Ti (Bi_2Ti_3) was found. No trace of Bi_3Ti_2 reported in the literature[6] was observed. It is possible that Vassilev[6] regarded $Bi_3Ti_2O_x$ as Bi_3Ti_2 since the quartz tubes were used as a container in his experiment.

Acknowledgments

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