Phase Relation in the Titanium-Rich Region of the Ge-Si-Ti Ternary System

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The Ti-rich region of the Ge-Si-Ti ternary isotherm at 900°C was determined by metallography, X-ray diffraction, and electron microprobe analysis. The sample alloys were prepared by arc-melting. It was confirmed that at 900°C Ti_5Si_3 and Ti_5Ge_3 form a continuous solid solution $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ with the hP16 crystal structure. The lattice constants for $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ are linear functions of the composition variable x . This continuous solid solution also exists at 1100°C. There is another solid solution $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, that has the same crystal structure as Ti_3Si (tP32), but this solid solution is stable only for $y \leq 0.44$ at 900°C. It was also shown that there is not any other binary or ternary phase within the Ti-Ti₅Si₃-Ti₅Ge₃ triangular region except $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$. In this region, there is one three-phase field $\text{Ti} + \text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3 + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, and the compositions of these three phases are $\text{Ti}_{0.96}\text{Si}_{0.03}\text{Ge}_{0.01}$, $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$, and $\text{Ti}_{0.75}\text{Si}_{0.14}\text{Ge}_{0.11}$ respectively. In addition, there are three two-phase fields within this region: $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3 + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, $\text{Ti} + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, and $\text{Ti} + \text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$.

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I. Introduction

Silicon-germanium alloys have been increasingly used in Si-based electronic devices to increase the device performance⁽¹⁾⁽²⁾. As in conventional Si-based devices, the formation of stable metal-semiconductor interfaces in these SiGe-based devices is a key issue in device manufacturing. Titanium disilicide is a strong candidate for the metallization contact material. One approach of forming the TiSi_2 layer is through the solid-state reaction of Ti with SiGe films. An experimental Ge-Si-Ti phase diagram will be very helpful for understanding the solid-state reaction between Ti and SiGe.

The three constituent binary phase diagrams for Ge-Si-Ti can be found in the literature, and are all well established⁽³⁾⁻⁽⁶⁾. However, the literature on the Ge-Si-Ti ternary phase diagram is very scarce, and is limited to the SiGe-rich region. Only the trapezoid region delineated by pure Si, pure Ge, TiGe_2 , and TiSi_2 had been studied (Fig. 1)⁽⁷⁾⁽⁸⁾. The two compounds TiGe_2 and TiSi_2 have the same crystal structure (oF24) and very similar lattice constants (within 6%)⁽⁴⁾⁽⁵⁾. As a consequence, they form a continuous solid solution at 900°C⁽⁸⁾, and possibly at other temperatures. Germanium and Si also form a continuous solid solution at all temperatures⁽⁶⁾. Other than the TiGe_2 - TiSi_2 solid solution and the Ge-Si solid solution, there is not any binary or ternary phase within the Si-Ge-TiGe₂-TiSi₂ trapezoid region at 900°C. Between the two solid solutions is a two-phase field. The tie-lines for this two-phase field had been determined⁽⁸⁾. No other information on ternary phase equilibrium can be found

in the literature. The objective of this study is to experimentally determine the Ti-rich region of the Ge-Si-Ti ternary isotherm at 900°C.

According to the Ge-Ti binary phase diagram⁽⁶⁾, the most Ti-rich intermetallic compound is Ti_5Ge_3 . This compound has the hP16 structure (prototype Mn_5Si_3) with $a=0.7563(2)$, $c=0.5228(2)$ nm⁽⁵⁾. In the Si-Ti binary system, there is also a Ti_5Si_3 compound with the same hP16 structure and $a=0.74610(3)$ nm, $c=0.51508(1)$ nm.⁽⁹⁾ Since Ti_5Ge_3 and Ti_5Si_3 have the same crystal structure and very similar lattice constants (within 1.5%), it is expected that these two phases may form a

Fig. 1 The Ge-Si-Ti isotherm at 900°C (in atomic percent). The phases TiSi_2 and TiGe_2 form a continuous solid solution; Si and Ge also form a continuous solid solution. The thin straight lines between these two solid solutions are the tie-lines. The alloy compositions used in this study are labeled 1 to 10.

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continuous solid solution $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$. If this solid solution exists, this single phase field will then separate the Ge–Si–Ti isotherm into two regions, with one region that has Ti-content richer than 62.5 at% and one leaner than 62.5 at%. The scope of this study is limited to alloys with Ti-content that are equal to or higher than 62.5 at%. In addition to the two binary phases Ti_5Ge_3 and Ti_5Si_3 , there is another binary phase Ti_3Si with the tP32 structure (prototype Ti_3P) in the region of current interests⁽⁶⁾. No ternary compound has been reported in this region in the literature.

II. Experimental Procedure

Alloys with ten different compositions, numbered 1 to 10 and listed in **Table 1**, were prepared by arc-melting. The locations of these alloys on the Ge–Si–Ti diagram are marked in Fig. 1. These alloys were made from 99.9999% pure Si, 99.9999% pure Ge, and 99.99% pure Ti. The total mass of each alloy was about 0.6 g. These alloys were arc-melted with a non-consumable tungsten electrode in an Ar atmosphere. The arc-melting chamber was evacuated and back-filled with high-purity Ar several times before arc-melting to avoid O and N contamination. Each alloy was re-melted at least four times to en-

Table 1 Alloy compositions and the characterization results.

Alloy No.	Original composition (mole fraction)	Heat treatment	Metallography	XRD	EPMA (mole fraction)	Phase(s)	Remarks
1	$\text{Ti}_{0.625}\text{Si}_{0.275}\text{Ge}_{0.1}$	900°C 500 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.63}\text{Si}_{0.27}\text{Ge}_{0.10}$	$\text{Ti}_5(\text{Si}_{0.73}\text{Ge}_{0.27})_3$	Four small peaks are not identified in XRD. Some XRD peaks appear asymmetric or split into two peaks.
1H	$\text{Ti}_{0.625}\text{Si}_{0.275}\text{Ge}_{0.1}$	1100°C 311 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.63}\text{Si}_{0.27}\text{Ge}_{0.10}$	$\text{Ti}_5(\text{Si}_{0.73}\text{Ge}_{0.27})_3$	
2	$\text{Ti}_{0.625}\text{Si}_{0.1875}\text{Ge}_{0.1875}$	900°C 500 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.64}\text{Si}_{0.18}\text{Ge}_{0.18}$	$\text{Ti}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_3$	Some XRD peaks appear asymmetric or split into two peaks.
2H	$\text{Ti}_{0.625}\text{Si}_{0.1875}\text{Ge}_{0.1875}$	1100°C 311 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.64}\text{Si}_{0.18}\text{Ge}_{0.18}$	$\text{Ti}_5(\text{Si}_{0.5}\text{Ge}_{0.5})_3$	
3	$\text{Ti}_{0.625}\text{Si}_{0.1}\text{Ge}_{0.275}$	900°C 500 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.64}\text{Si}_{0.11}\text{Ge}_{0.25}$	$\text{Ti}_5(\text{Si}_{0.3}\text{Ge}_{0.7})_3$	Some XRD peaks appear asymmetric or split into two peaks.
3H	$\text{Ti}_{0.625}\text{Si}_{0.1}\text{Ge}_{0.275}$	1100°C 311 h	single phase	$\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$	$\text{Ti}_{0.64}\text{Si}_{0.10}\text{Ge}_{0.26}$	$\text{Ti}_5(\text{Si}_{0.28}\text{Ge}_{0.72})_3$	
4	$\text{Ti}_{0.7}\text{Si}_{0.25}\text{Ge}_{0.05}$	900°C 600 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	Ti $\text{Ti}_{0.63}\text{Si}_{0.32}\text{Ge}_{0.05}$ $\text{Ti}_{0.75}\text{Si}_{0.20}\text{Ge}_{0.05}$	Ti $\text{Ti}_5(\text{Si}_{0.86}\text{Ge}_{0.14})_3$ $\text{Ti}_3(\text{Si}_{0.8}\text{Ge}_{0.2})$	The amount of Ti is very small, and Ti could disappear completely upon longer annealing. (compare alloys 4 & 4S)
4S	$\text{Ti}_{0.7}\text{Si}_{0.25}\text{Ge}_{0.05}$	900°C 300 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	Ti $\text{Ti}_{0.63}\text{Si}_{0.33}\text{Ge}_{0.04}$ $\text{Ti}_{0.75}\text{Si}_{0.19}\text{Ge}_{0.06}$	Ti $\text{Ti}_5(\text{Si}_{0.89}\text{Ge}_{0.11})_3$ $\text{Ti}_3(\text{Si}_{0.76}\text{Ge}_{0.24})$	The amount of Ti is large compared to alloy 4.
5	$\text{Ti}_{0.75}\text{Si}_{0.2}\text{Ge}_{0.05}$	900°C 600 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	? $\text{Ti}_{0.63}\text{Si}_{0.32}\text{Ge}_{0.05}$ $\text{Ti}_{0.74}\text{Si}_{0.21}\text{Ge}_{0.05}$	Ti $\text{Ti}_5(\text{Si}_{0.86}\text{Ge}_{0.14})_3$ $\text{Ti}_3(\text{Si}_{0.81}\text{Ge}_{0.19})$	Similar to alloy 6. Probably is a non-equilibrium alloy, and is single-phase $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ at equilibrium.
6	$\text{Ti}_{0.75}\text{Si}_{0.15}\text{Ge}_{0.1}$	900°C 600 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.97}\text{Si}_{0.01}\text{Ge}_{0.02}$ $\text{Ti}_{0.63}\text{Si}_{0.31}\text{Ge}_{0.06}$ $\text{Ti}_{0.75}\text{Si}_{0.15}\text{Ge}_{0.10}$	Ti $\text{Ti}_5(\text{Si}_{0.84}\text{Ge}_{0.16})_3$ $\text{Ti}_3(\text{Si}_{0.60}\text{Ge}_{0.40})$	The amount of $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ is more than that in alloy 6S. Probably is a non-equilibrium alloy, and is single-phase $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ at equilibrium.
6S	$\text{Ti}_{0.75}\text{Si}_{0.15}\text{Ge}_{0.1}$	900°C 300 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.98}\text{Si}_{0.01}\text{Ge}_{0.01}$ $\text{Ti}_{0.63}\text{Si}_{0.31}\text{Ge}_{0.06}$ $\text{Ti}_{0.75}\text{Si}_{0.15}\text{Ge}_{0.10}$	Ti $\text{Ti}_5(\text{Si}_{0.84}\text{Ge}_{0.16})_3$ $\text{Ti}_3(\text{Si}_{0.60}\text{Ge}_{0.40})$	The amounts of Ti and $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ are more than those in alloy 6. Probably is a non-equilibrium alloy, and is single-phase $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ at equilibrium.
7	$\text{Ti}_{0.75}\text{Si}_{0.1}\text{Ge}_{0.15}$	900°C 600 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.96}\text{Si}_{0.03}\text{Ge}_{0.01}$ $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$ $\text{Ti}_{0.75}\text{Si}_{0.14}\text{Ge}_{0.11}$	Ti $\text{Ti}_5(\text{Si}_{0.22}\text{Ge}_{0.78})_3$ $\text{Ti}_3(\text{Si}_{0.56}\text{Ge}_{0.44})$	
8	$\text{Ti}_{0.75}\text{Si}_{0.05}\text{Ge}_{0.2}$	900°C 300 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.96}\text{Ge}_{0.04}$ $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$?	Ti $\text{Ti}_5(\text{Si}_{0.22}\text{Ge}_{0.78})_3$ $\text{Ti}_3(\text{Si}_7\text{Ge}_7)$	
9	$\text{Ti}_{0.8}\text{Si}_{0.1}\text{Ge}_{0.1}$	900°C 500 h	three phase	Ti $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.98}\text{Si}_{0.01}\text{Ge}_{0.01}$? $\text{Ti}_{0.76}\text{Si}_{0.13}\text{Ge}_{0.11}$	Ti $\text{Ti}_5(\text{Si}_7\text{Ge}_7)_3$ $\text{Ti}_3(\text{Si}_{0.54}\text{Ge}_{0.46})$	
10	$\text{Ti}_{0.85}\text{Si}_{0.1}\text{Ge}_{0.05}$	900°C 300 h	two phase	Ti $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$	$\text{Ti}_{0.98}\text{Si}_{0.01}\text{Ge}_{0.01}$ $\text{Ti}_{0.76}\text{Si}_{0.16}\text{Ge}_{0.08}$	Ti $\text{Ti}_3(\text{Si}_{0.67}\text{Ge}_{0.33})$	

sure homogeneity. Each alloy was then weighted again to monitor weight change during the arc-melting. In every case, the weight decrease was negligible to change the alloy composition. Each alloy was then sealed in an evacuated (700 mPa) quartz tube, and heat treated at 900°C. The annealing times for the alloys are given in Table 1. Alloys 1H, 2H, and 3H, which have the same compositions as alloy 1, 2 and 3 respectively, were annealed at 1100°C, instead of 900°C.

After annealing, each alloy was sectioned into two halves by a low-speed diamond saw, with one half polished for metallographic examination and electron-microprobe analysis (EPMA), and the other half ground into powder for X-ray powder diffraction measurement (XRD). An electron-microprobe, operated at 15 keV, was used to determine the phase compositions. The measured X-ray was $K\alpha$ in each case, and the standards used were pure Si, Ge, and Ti respectively. In microprobe measurement, the concentrations of Si, Ge, and Ti were measured independently, and the total weight percentage was within $100 \pm 1\%$ in each case. For every phase, at least four measurements were made and the average value was reported. Care had been taken to ensure that the grains being measured were large enough in size to avoid generating and collecting signals from the neighboring grains. It was estimated that the accuracy of EPMA measurements is better than 2 at%. The XRD measurements were done on a diffractometer using the Cu $K\alpha_1$ radiation. In measuring the lattice constants, Si powder was added to serve as the internal standard.

III. Results and Discussion

The characterization results of this study are summarized in Table 1. These results lead to the isotherm shown in Fig. 2. The region between the Ti_5Si_3 - Ti_5Ge_3 line and the $TiSi_2$ - $TiGe_2$ line is still undetermined, and is left blank. There is a continuous solid solution $Ti_5(Si_{1-x}Ge_x)_3$ between Ti_5Si_3 and Ti_5Ge_3 at 900°C (and 1100°C). This solid solution is represented by a heavy solid line connecting Ti_5Si_3 and Ti_5Ge_3 . There is a three-phase region $Ti + Ti_5(Si_{0.22}Ge_{0.78})_3 + Ti_3(Si_{0.56}Ge_{0.44})$ above this solid solution. The compound Ti_3Si can dissolve some Ge to become a solid solution $Ti_3(Si_{1-y}Ge_y)$, but the stability range for this solid solution is limited since there is no stable Ti_3Ge . The rest of the region includes three two-phase fields: $Ti_5(Si_{1-x}Ge_x)_3 + Ti_3(Si_{1-y}Ge_y)$, $Ti + Ti_3(Si_{1-y}Ge_y)$, and $Ti + Ti_5(Si_{1-x}Ge_x)_3$. The thin lines passing through alloys 4 and 10 are tie-lines for the two-phase regions. A discussion of the experimental results and their relations to Fig. 2 is presented below.

It is confirmed by metallography and XRD of alloys 1-3 that Ti_5Si_3 and Ti_5Ge_3 form a continuous solid solution $Ti_5(Si_{1-x}Ge_x)_3$ at 900°C. From metallographic observations, alloys 1-3 have very similar microstructures, and only one phase was observed. Figures 3(a) and (b) are an optical micrograph and a secondary electron micrograph respectively for alloy 2. The dark grain boundaries in Fig. 3(a) are not the precipitates of a sec-

Fig. 2 The experimentally determined Ge-Si-Ti isotherm at 900°C (in atomic percent). There is a continuous solid solution between Ti_5Si_3 and Ti_5Ge_3 . The thin lines passing through alloys 4 and 10 are tie-lines for the two phase regions.

Fig. 3 (a) An optical micrograph for alloy 2. This alloy is a single-phase $Ti_5(Si_{1-x}Ge_x)_3$. The dark grain boundaries are not precipitates of a second phase, but are optical artifacts due to de-focus of the image. (b) A secondary electron micrograph for the same alloy.

Fig. 4 X-ray powder diffraction patterns for alloys 1, 2 and 3. All the peaks, except those marked with “?”, are from hP16 $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$. The source for these small peaks is unclear. Some of the peaks appear asymmetric or split into two peaks. This indicates that alloys 1–3 have not reached complete homogeneity in composition. The radiation used was $\text{Cu K}\alpha_1$.

ond phase, but are optical artifacts due to de-focus of the image. The sample was etched with a 50 vol% $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$ solution to enhance the contrast, and this etching removed materials from the grain boundaries and made the grain boundaries not level with the grains. Figure 3(b) shows that there is no second phase at the grain boundaries. **Figure 4** shows the XRD patterns for alloys 1, 2, and 3. All the peaks, except those marked with “?”, are from a phase with the hP16 structure, as is the case with that of Ti_5Si_3 or Ti_5Ge_3 . This suggests the existence of a solid solution phase $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ with the hP16 structure. In Fig. 4, some of the peaks appear asymmetric or split into two peaks. This indicates that alloys 1–3 have not reached complete homogeneity in composition. This is probably because the annealing temperature was low compared to the melting temperature of Ti_5Si_3 (2130°C) and Ti_5Ge_3 (1980°C), and a much longer annealing time is required to bring these alloys to homogeneity in composition. Moreover, in alloy 1 of Fig. 4, there are four very small peaks (marked with “?”) that cannot be attributed to any apparent phase. As more Ge atoms are incorporated into $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, the lattice constants increase due to the larger Ge atom size compared to that of Si. As can be seen in Fig. 4, this increase in unit cell dimension makes the diffraction peaks shift toward lower 2θ . The lattice constants a and c for alloys 1, 2, and 3 are plotted against x in Fig. 5(a) and (b) respectively. The lattice constants for pure Ti_5Si_3 and Ti_5Ge_3 are taken from the literature⁽⁵⁾⁽⁹⁾. As can be seen in Fig. 5, the lattice constants are linear functions of the composition, and therefore follow Vegard’s law. From EPMA measurements (Table 1), it was found that the compositions of the alloys after annealing were essentially the same as the starting compositions, indicating there was no material loss during sample preparation and analysis. Although the asymmetric peaks and peak-splitting in XRD suggest that there is a certain degree of inhomogeneity in compositions, the EMPA measure-

Fig. 5 The lattice constants a and c of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ as a function of the composition variable x .

ments did not detect any appreciable difference in composition at different locations on the samples. This is probably because the composition difference is smaller than the accuracy of EPMA (about one or two at%).

The $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ solid solution exists not only at 900°C, but also at 1100°C. This is supported by the results from alloys 1H, 2H and 3H which were annealed at 1100°C. The metallography, XRD, and EPMA results of these alloys were the same as those of alloys 1, 2 and 3, except that the extent of asymmetric peaks and peak-splitting in XRD was less apparent.

According to the Ti–Si and the Ti–Ge binary phase diagrams⁽⁶⁾, Ti_5Si_3 has a range of homogeneity as wide as 4 at% while Ti_5Ge_3 is a line compound. In this study, we did not attempt to determine the range of homogeneity for the solid solution phase $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$. In Fig. 2, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ is represented by a heavy line, but it should be stressed that the actual homogeneity of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ might be wider than this line at some compositions.

Alloys 4 and 4S have the same composition, but alloy 4S was annealed for a shorter time (300 h, compared to 600 h for alloy 4). The XRD pattern for alloy 4 is shown in Fig. 6. Diffraction peaks from three phases, Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, were present. From the relative peak heights, one can conclude that the amount of Ti is quite small. The compound $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ has the same crystal structure as that of Ti_3Si (tP32, prototype Ti_3P). **Figures 7(a)** and **(b)** are optical micrographs for alloy 4S and 4 respectively. Three phases, Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ are present in both micrographs, but the amount of Ti in alloy 4 is much

Fig. 6 The XRD pattern for alloy 4. The diffraction peaks from hP16 $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and tP32 $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ are identified. In addition, there are three small peaks from Ti. The radiation used was $\text{Cu K}\alpha_1$.

Fig. 7 (a) An optical micrographs for alloy 4S (300 h). (b) An optical micrographs for alloy 4 (600 h). In both micrographs, three phases, Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ are present, but the amount of Ti in alloy 4 is much smaller compared to that in alloy 4S. This observation suggests that Ti is possibly not an equilibrium phase and will eventually disappear upon further annealing.

smaller compared to that in alloy 4S. This observation leads us to assume that Ti is not an equilibrium phase at this composition and will eventually disappear completely upon longer annealing. In other words, the

equilibrium phases at this composition are probably only $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$. The compositions for $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ in alloy 4, determined by using EPMA, are $\text{Ti}_{0.63}\text{Si}_{0.32}\text{Ge}_{0.05}$ and $\text{Ti}_{0.75}\text{Si}_{0.20}\text{Ge}_{0.05}$ respectively. These two compositions correspond to $\text{Ti}_5(\text{Si}_{0.86}\text{Ge}_{0.14})_3$ and $\text{Ti}_3(\text{Si}_{0.8}\text{Ge}_{0.2})$ respectively. Since the amount of Ti in alloy 4 is quite small, we can assume that the compositions for alloy 4 are very close to the tie-line composition for an equilibrium alloy with the same overall composition. The tie-line determined this way is shown in Fig. 2 as a thin line. As can be seen in Fig. 2, this tie-line passes through the composition point of the starting alloy, indicating that the assumption is reasonable. In the Ti-Ge binary system, there is no stable Ti_3Ge phase like Ti_3Si , but the existence of $\text{Ti}_3(\text{Si}_{0.8}\text{Ge}_{0.2})$ indicates that Ti_3Si is able to dissolve some Ge. The extent of Ge solubility in Ti_3Si will be established in the discussion for alloys 7 and 9.

Alloy 5 is very similar in microstructure to alloys 6 (600 h) and 6S (300 h), and these three alloys are all three-phase mixture of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3 + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y) + \text{Ti}$ according to the metallography and XRD results. **Figures 8(a) and (b)** are the optical micrographs for alloys 6S and 6, respectively. It can be seen that the amounts of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and Ti in alloy 6 are less than those in alloy 6S. In other words, longer annealing reduced the amounts of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and Ti, and increased the amount of $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$. This leads us to assume that alloys 6, 6S, and 5 are non-equilibrium alloys. At equilibrium, these alloys probably would be single-phase $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$. The compositions determined by EPMA are given in Table 1. It is worth noting that, in alloys 5, 6, and 6S, the compositions of the $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ phase are nearly the same as the original alloy compositions. From the results of alloy 4, it had been established that $\text{Ti}_3(\text{Si}_{0.8}\text{Ge}_{0.2})$ is stable, but the original composition of alloy 5 is exactly $\text{Ti}_3(\text{Si}_{0.8}\text{Ge}_{0.2})$. In other words, alloy 5 is located in the $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ single-phase field. Moreover, according to the results for alloy 7 and 9 (see below), the compound $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ is stable for y as high as 0.44. Since the original composition of alloy 6 (and 6S) has a y value smaller than 0.44, alloy 6 (and 6S) is also within the $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ single-phase field. These observations also lead us to consider alloys 5, 6, and 6S non-equilibrium alloys. In Fig. 2, we have assumed that alloys 5, 6, and 6S are all within the $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ single-phase field. In the Si-Ti binary system, there is a peritectoid $\text{Ti} + \text{Ti}_5\text{Si}_3 = \text{Ti}_3\text{Si}$ at 1170°C . This invariant reaction is probably the reason why alloys 5, 6 and 6S had such a difficulty in reaching equilibrium.

Alloy 7 is a three-phase mixture of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, and Ti. **Figure 9** is a secondary electron micrograph for this alloy. The microstructure has the characteristics of an alloy having reached its equilibrium state, *i.e.* smooth and round phase boundaries. The compositions for these three phases are $\text{Ti}_{0.96}\text{Si}_{0.03}\text{Ge}_{0.01}$, $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$, and $\text{Ti}_{0.75}\text{Si}_{0.14}\text{Ge}_{0.11}$. These three compositions provide a guide for locating the three vertices of the tie-triangle.

Fig. 8 (a) An optical micrographs for alloy 6S (300 h). (b) An optical micrographs for alloy 6 (600 h). In both micrographs, three phases, Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ are present, but the amounts of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and Ti in alloy 6 is less than those in alloy 6S. In other words, longer annealing reduced the amounts of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and Ti, and increased the amount of $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$. This leads us to assume that alloys 6 and 6S are non-equilibrium alloys.

Figure 10 is an optical micrograph for alloy 8. The three phases present are Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ according to the XRD result. The amount of $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ is small compared to the other two phases, indicating this alloy is close to the phase boundary of the tie-triangle. The compositions for Ti and $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ are determined to be $\text{Ti}_{0.96}\text{Ge}_{0.04}$ and $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$ respectively. These two compositions have two of the three vertices of the tie-triangle. These two compositions are very close to the corresponding ones for alloy 7. The composition of $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ could not be determined accurately since its particle sizes are too small for accurate EPMA measurement.

Figure 11 is a secondary electron micrograph for alloy 9. In addition to Ti and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, there is a small amount of $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ present in this alloy, suggesting that this alloy is very close to the Ti + $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ two-phase field. Alloy 9 has excellent mechanical properties. It is very tough and has a Vickers hardness of 630HV (1 kg load). Alloys 7, 8 and 9 are all in the three-phase field. Based on the EPMA results from these three alloys, we estimate the compositions of the three

Fig. 9 Secondary electron micrograph for alloy 7. The three co-existing phases are Ti, $\text{Ti}_5(\text{Si}_{0.56}\text{Ge}_{0.44})_3$, and $\text{Ti}_5(\text{Si}_{0.22}\text{Ge}_{0.78})_3$.

Fig. 10 Optical micrograph for alloy 8. The three co-existing phases are Ti, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$.

Fig. 11 Secondary electron micrograph for alloy 9. This alloy is a three-phase mixture of Ti + $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ + $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$.

vertices of the tie-triangle are $\text{Ti}_{0.96}\text{Si}_{0.03}\text{Ge}_{0.01}$, $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$, and $\text{Ti}_{0.75}\text{Si}_{0.14}\text{Ge}_{0.11}$.

Alloy 10 shown in **Fig. 12** is clearly two-phase. The XRD measurement confirmed that it is a Ti +

Fig. 12 Optical micrograph of alloy 10. The co-existing phases are Ti and $\text{Ti}_3(\text{Si}_{0.67}\text{Ge}_{0.33})$.

$\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ two-phase alloy. The compositions of these two phases are $\text{Ti}_{0.98}\text{Si}_{0.01}\text{Ge}_{0.01}$ and $\text{Ti}_{0.76}\text{Si}_{0.16}\text{Ge}_{0.08}$ according to the EPMA measurement. From these two compositions, a tie-line can be established for the $\text{Ti} + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ two-phase region. This tie-line is shown in Fig. 2 with a thin line. As can be seen in this figure, this tie-line passes through the composition point of the starting alloy, indicating no material was lost during the arc-melting and other processing steps.

IV. Summary

It was confirmed that at 900°C Ti_5Si_3 and Ti_5Ge_3 form a continuous solid solution $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ with the hP16 crystal structure (Fig. 2). The lattice constants for $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ are linear functions of the composition

variable x . This continuous solid solution also exists at 1100°C . There is another solid solution $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$ that has the same crystal structure as Ti_3Si (tP32), but this solid solution is stable only for $y \leq 0.44$ at 900°C . It is also shown that, other than $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$ and $\text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, there is neither binary nor ternary phase within the $\text{Ti}-\text{Ti}_5\text{Si}_3-\text{Ti}_5\text{Ge}_3$ triangular region. There is one three-phase field $\text{Ti} + \text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3 + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, and the compositions of the three vertices of the tie-triangle are $\text{Ti}_{0.96}\text{Si}_{0.03}\text{Ge}_{0.01}$, $\text{Ti}_{0.63}\text{Si}_{0.08}\text{Ge}_{0.29}$, and $\text{Ti}_{0.75}\text{Si}_{0.14}\text{Ge}_{0.11}$, respectively. In addition, there are three binary phase fields: $\text{Ti} + \text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3$, $\text{Ti}_5(\text{Si}_{1-x}\text{Ge}_x)_3 + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$, and $\text{Ti} + \text{Ti}_3(\text{Si}_{1-y}\text{Ge}_y)$.

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