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Isothermal Section of the Ti-Si-B System at 1250 °C in the Ti-$TiSi_2$-TiB_2 Region

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A partial isothermal section (Ti-$TiSi_2$-TiB_2 region) of the ternary Ti-Si-B system at 1250 °C was determined from heat-treated alloys prepared via arc melting. Microstructural characterization has been carried out through scanning electron microscopy (SEM), X-ray diffraction (XRD) and wavelength dispersive spectrometry (WDS). The results have shown the stability of the near stoichiometric Ti_6Si_2B phase and a negligible solubility of boron in the Ti-silicides as well as of Si in the Ti-borides. The following three-phase equilibria have been observed in the Ti- $TiSi_2$-TiB_2 region: Ti_{ss}+TiB+Ti_6Si_2B, Ti_{ss}+Ti_6Si_2B+Ti_5Si_3, Ti_5Si_3+Ti_6Si_2B+TiB, Ti_5Si_3+TiB+Ti_3B_4, Ti_5Si_3+Ti_3B_4+TiB_2, Ti_5Si_3+TiB_2+Ti_5Si_4, Ti_5Si_4+TiB_2+TiSi and TiSi+TiB_2+$TiSi_2$.

Keywords: *Ti-Si-B system, titanium alloys, phase diagram, isothermal section, phase equilibria*

1. Introduction

Initial information on phase equilibria in the Ti-Si-B system was provided by Meschter[1] and Maex et al.[2] from thermodynamic calculations, using data from the binary phases of the Ti-B and Ti-Si systems. Figure 1a,b shows the isothermal sections calculated by these authors.

From experimental results, Ramos et al.[3,4] showed the existence of a stable ternary phase with Ti_6Si_2B stoichiometry in this system. Additionally, the phase relations involving this phase at 1250 °C and its formation reaction from the liquid state were also showed. Yang et al.[5] carried out a thermodynamic calculation of the Ti-Si-B system, proposing a liquidus projection and an isothermal section at 1250 °C from selected experiments and the results from Ramos et al.[3,4]. The experiments carried out by Yang et al.[5] involved the production by arc-melting, annealing at 1250 °C for 100h and microstructural characterization of four samples of composition Ti-21Si-10B, Ti-19Si-6B, Ti-16.5Si-3.5B and Ti-14Si-1B. All these compositions are located in the Ti-rich region of the Ti-Si-B system, specifically in the βTi+Ti_5Si_3+Ti_6Si_2B three-phase field of this system at 1250 °C.

In order to extend the phase stability knowledge of this system, this work evaluated the phase relations in the Ti-$TiSi_2$-TiB_2 region of the Ti-Si-B system at 1250 °C and the results were compared with those from Yang et al.[5].

2. Experimental Procedure

Several ingots (~ 8 g) of different compositions were produced from high-purity commercially available materials: titanium (99.8 % min.), silicon (99.999 % min.) and boron (99.5 % min.). Table 1 shows the nominal compositions of the alloys used in this work. The samples were prepared via arc-melting with a non-consumable tungsten electrode on a water-cooled hearth under high purity argon atmosphere gettered by titanium. The ingots were melted five times in an effort to produce homogeneous alloys. Then, parts of the as-cast ingots were heat-treated at 1250 °C for up to 240 h under argon in quartz tubes. In order to confirm the stability of the Ti_3B_4 and support some proposed phase relations which could not be experimentally proved, a $Ti_{42.89}B_{57.11}$ (Ti_3B_4 stoichiometry) alloy was arc-melted and heat-treated at 1250 °C for 30 days and at 1500 °C for 55 h.

All the samples were characterized by scanning electron microscopy (SEM) and selected alloys were evaluated via microanalysis wavelength dispersive spectrometry (WDS).

The SEM/BSE images were acquired in a LEO 1450VP SEM equipment. The WDS measurements were carried out in a model 440 Stereoscan/Leica Microscope at 15 kV/10 nA using PET and LSM 200 crystals to quantify the contents of Ti/Si and B, respectively. Pure elements were used as standards, and the results were obtained using a ϕρz correction procedure. At least three measurements for each phase were carried out.

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3. Results and Discussion

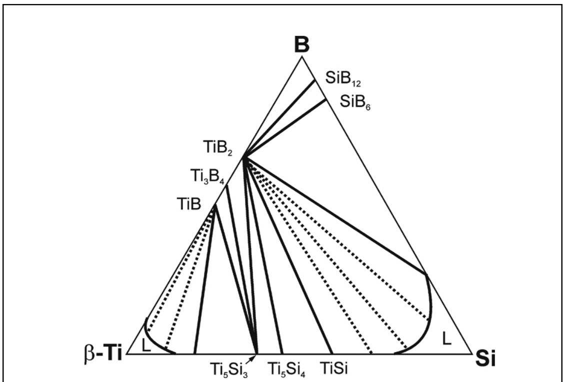
Figure 2 shows the partial isothermal section at 1250 °C of the Ti-Si-B system determined in this work. Data for the binaries Ti-Si and Ti-B systems were taken from[6] and includes the following phases: Ti_{ss}, Ti_5Si_3, Ti_5Si_4, TiSi, $TiSi_2$, TiB, Ti_3B_4 and TiB_2. There exists only one ternary phase, Ti_6Si_2B, which was discovered by Ramos et al.[4] and is isotypic with Ni_6Si_2B.

The WDS measurements data can be roughly evaluated via the measured values of B and Si in the borides and silicides present in Table 1. These borides and silicides are near stoichiometric phases in the correspondent binaries phase diagrams. For TiB, the concentration of B should be near 50 at.% and the measured values were in the range of 52.6 to 54.3 at.% B. For TiB_2, it is expected 66.7 at.% B and the measured values were in the range of 65.6 to 69.1 at.% B. For Ti_5Si_3, the concentration of Si should be near 37.5 at.%, the measured values are in the range of 34 to 37.9 at.% Si, however, in this case, some solubility range might exist. For Ti_5Si_4, the concentration of Si should be near 40 at.%, the measured values are in the range of 40.8 to 43 at.% Si. For TiSi, the concentration of Si should be near 50 at.%, the measured values varied from 47 to 50.2 at.% Si. For $TiSi_2$, the concentration of Si should be 66.7 at.%, the measured value is 66.3 at.% Si.

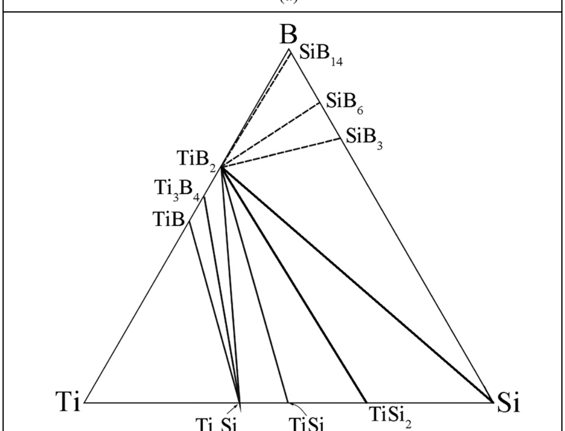
The microstructural characteristics of the alloys which allowed the establishment of the isothermal section shown in Figure 2 are presented below.

Alloy #40 ($Ti_{65}Si_{32.5}B_{2.5}$) presented Ti_{ss}, Ti_5Si_3 and Ti_6Si_2B phases in the as-cast as well as in the heat-treated samples. Figure 3a shows a SEM/BSE micrograph of this alloy in the heat-treated condition where Ti_{ss} and Ti_6Si_2B are minor phases in a Ti_5Si_3 matrix. The WDS results shown in Table 2 indicate a low solubility of Si and B in Ti_{ss} as well as of B in Ti_5Si_3. The cracks present in the Ti_5Si_3 phase (Figure 3a) are formed during cooling in the solid state, associated with the high anisotropy of thermal expansion of this phase[7].

Alloy # 55 ($Ti_{70}Si_{7.5}B_{22.5}$) presented Ti_{ss}, TiB and Ti_6Si_2B phases in the as-cast as well as in the heat-treated samples. Figure 3b shows a SEM/BSE micrograph of the heat-treated alloy where all the phases are present in significant amounts. The WDS data (Table 2) shows once again the low solubility of Si and B in Ti_{ss} as well as of Si in TiB. In addition, because the compositions of the Ti_{ss} and Ti_6Si_2B phases in the alloys #40 and #55 are approximately the same



(a)



(b)

Figure 1. Calculated isothermal section of the Ti-Si-B system at (a) 1600 °C[1]; (b) 727 °C[2].

Table 1. Nominal composition of the Ti-Si-B alloys used in this work.

Alloy #	Ti (at.%)	Si (at.%)	B (at.%)
14	66.7	22.2	11.1
40	65	32.5	2.5
46	55	40	5
55	70	7.5	22.5
69	60	25	15
77	50	45	5
79	40	50	10
91	53	17	30
92	47	13	40
93	51	19	30

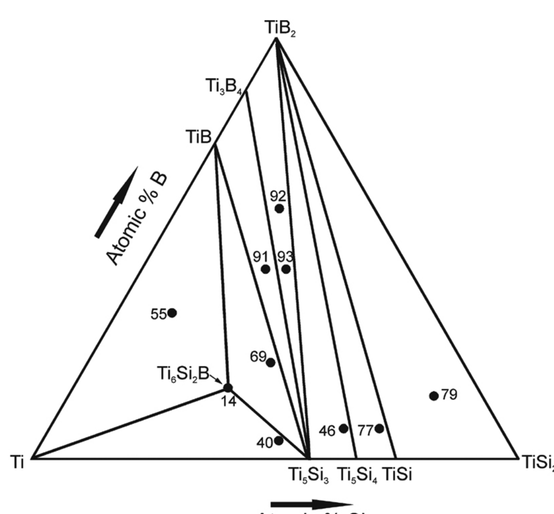


Figure 2. Isothermal section of the Ti-Si-B system at 1250 °C in the Ti-$TiSi_2$-TiB_2 region from results of this work.

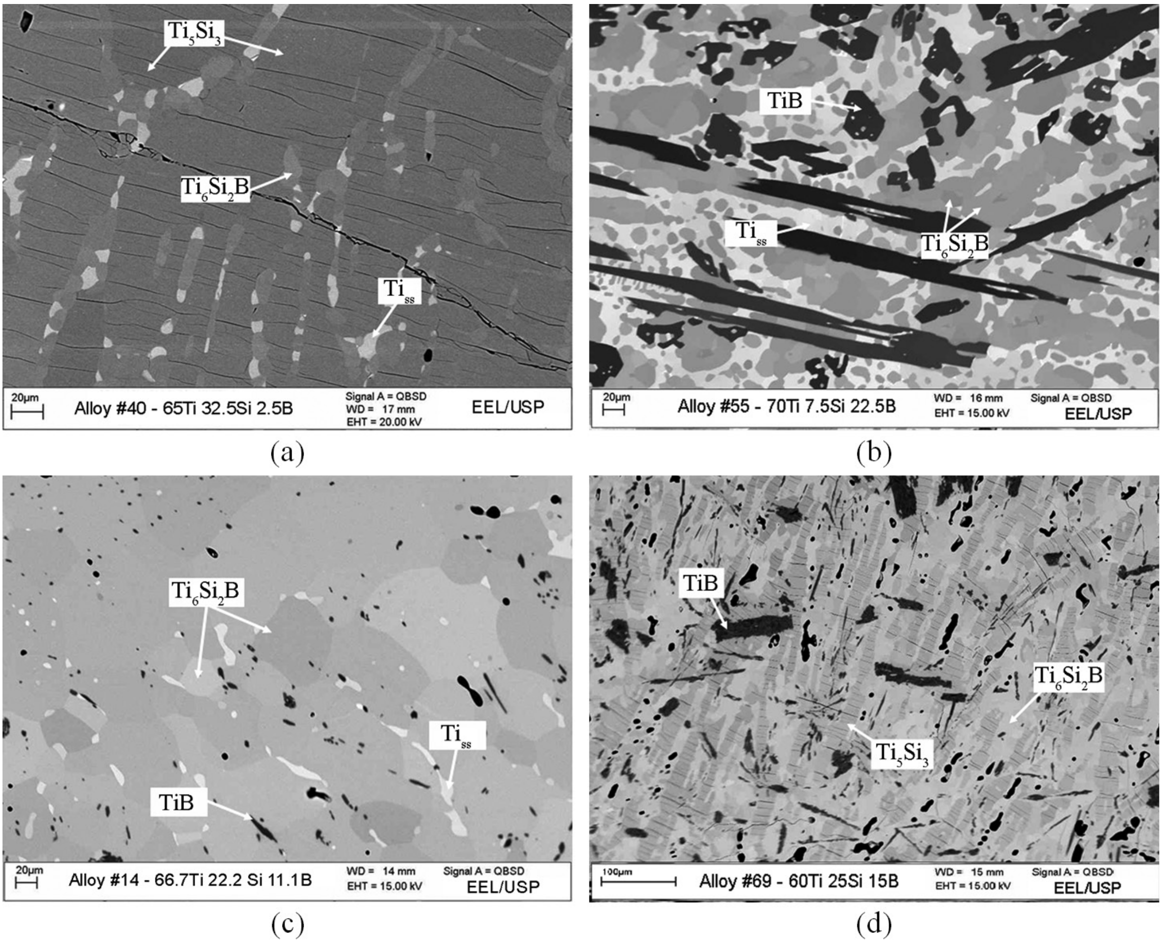


Figure 3. SEM/BSE micrographs from heat-treated Ti-Si-B alloys: (a) #40 (65Ti-32.5Si-2.5B); (b) #55 (70Ti-7.5Si-22.5B); (c) #14 (66.7Ti-22.2Si-11.1B); (d) #69 (60Ti-25Si-15B).

(Table 2), the Ti_{ss}+Ti_6Si_2B two-phase region should be quite narrow at 1250 °C.

The calculated results of Yang et al.[5] have shown some solubility of Si in the Ti_{ss} at 1250 °C. However, considering the low solubility of Si and B in Ti_{ss}, the low solubility of B and Si in the silicides and borides respectively, as well as the difficult to accurately determine the concentration of boron, we have not included any solubility data in Figure 2.

Alloy #14 ($Ti_{66.7}Si_{22.2}B_{11.1}$) presents the nominal composition of the stoichiometric Ti_6Si_2B phase. Five phases were observed in the as-cast sample: TiB_2, TiB, Ti_6Si_2B, Ti_5Si_3 and Ti_{ss}. After heat-treatment at 1250 °C, the microstructure formed was essentially constituted of the Ti_6Si_2B, with minor amount of Ti_{ss} and TiB, as shown in Figure 3c. These results suggested that the Ti_6Si_2B should be near stoichiometry at 1250 °C. Contrasting to the behavior observed for the samples with high volume fraction of Ti_5Si_3 phase, no crack was noticed in the Ti_6Si_2B phase, likely due to its lower thermal expansion anisotropy[7].

Alloy # 69 ($Ti_{60}Si_{25}B_{15}$) presented Ti_{ss}, Ti_5Si_3, TiB, TiB_2 and Ti_6Si_2B in the as-cast and TiB, Ti_5Si_3 and Ti_6Si_2B in the heat-treated sample, showing the complete dissolution of TiB_2 and Ti_{ss} during heat-treatment. Figure 3d shows a SEM/BSE micrograph of the heat-treated alloy. The WDS analysis shows very low solubility of B in the Ti_5Si_3 phase as well as of Si in the TiB phase.

As can be concluded from the previous results, at 1250 °C the ternary Ti_6Si_2B phase equilibrates with Ti_{ss}, TiB, and Ti_5Si_3 phases through narrow two-phase fields.

Alloy # 46 ($Ti_{55}Si_{40}B_5$) presented Ti_5Si_3, Ti_5Si_4, TiSi, $TiSi_2$ and TiB_2 in the as-cast and Ti_5Si_3 Ti_5Si_4 e TiB_2 in the heat-treated sample, indicating the dissolution of TiSi and $TiSi_2$ during the heat-treatment. Figure 4a shows a SEM/BSE micrograph of this alloy after heat-treatment. The WDS results show the low solubility of B in both Ti_5Si_3 and Ti_5Si_4 as well as of Si in TiB_2.

Alloy #77 ($Ti_{50}Si_{45}B_5$) presented Ti_5Si_4, TiSi, $TiSi_2$ and TiB_2 in the as-cast and Ti_5Si_4, TiSi and TiB_2 in the heat-treated sample, showing the dissolution of the $TiSi_2$ phase during the heat-treatment. Figure 4b shows a SEM/BSE micrograph of this alloy after heat-treatment where all the phases are present in significant amount. The WDS analysis from the Ti_5Si_4 and TiSi phases has shown a very low B solubility in these phases as well as of Si in TiB_2.

Table 2. Ti, Si and B contents of the phases present in the Ti-Si-B alloys measured by WDS analysis. Note that the composition ranges correspond to the minimum and maximum measured values.

Alloy #	Phase	Ti (at.%)	Si (at.%)	B (at.%)
40	Ti_{ss}	97.3-98.7	0.9-1.4	0.5-1.3
	Ti_5Si_3	62.9-63.7	35.6-37.1	0-0.7
	Ti_6Si_2B	63.8-65.1	22.5-22.8	12.4-13.4
55	Ti_{ss}	98.4-99.6	0.5-0.6	0.3-0.9
	TiB	46.5-46.8	0.1	53.1-53.4
	Ti_6Si_2B	67.1-67.9	19.8-20.0	12.1-13.1
14	Ti_{ss}	98.4-99.4	0.8-0.7	0.8-0
	Ti_6Si_2B	61.4-65.0	23.2-22.6	15.4-12.4
	TiB	45.3-47.6	nd	54.6-52.3
69	Ti_5Si_3	62.1	37.8-37.9	0-0.1
	TiB	45.7-47.4	0-0.1	52.6-54.3
	Ti_6Si_2B	63.6-64.9	23.2-23.3	11.9-13.2
46	Ti_5Si_3	64.4-64.7	34.0-34.4	1.0-1.7
	Ti_5Si_4	58.7-59.1	40.8-41.3	nd
	TiB_2	32.0-34.3	0-0.1	65.6-68.0
77	Ti_5Si_4	57.0-57.9	42.1-43.0	nd
	TiSi	52.5-53.0	47.0-47.5	nd
	TiB_2	32.3-33.4	0-0.1	66.6-67.7
79	TiSi	49.9	50.0-50.2	nd
	$TiSi_2$	33.7	66.3	nd
	TiB_2	30.8-32.2	0.1	67.8-69.1

nd – not detected.

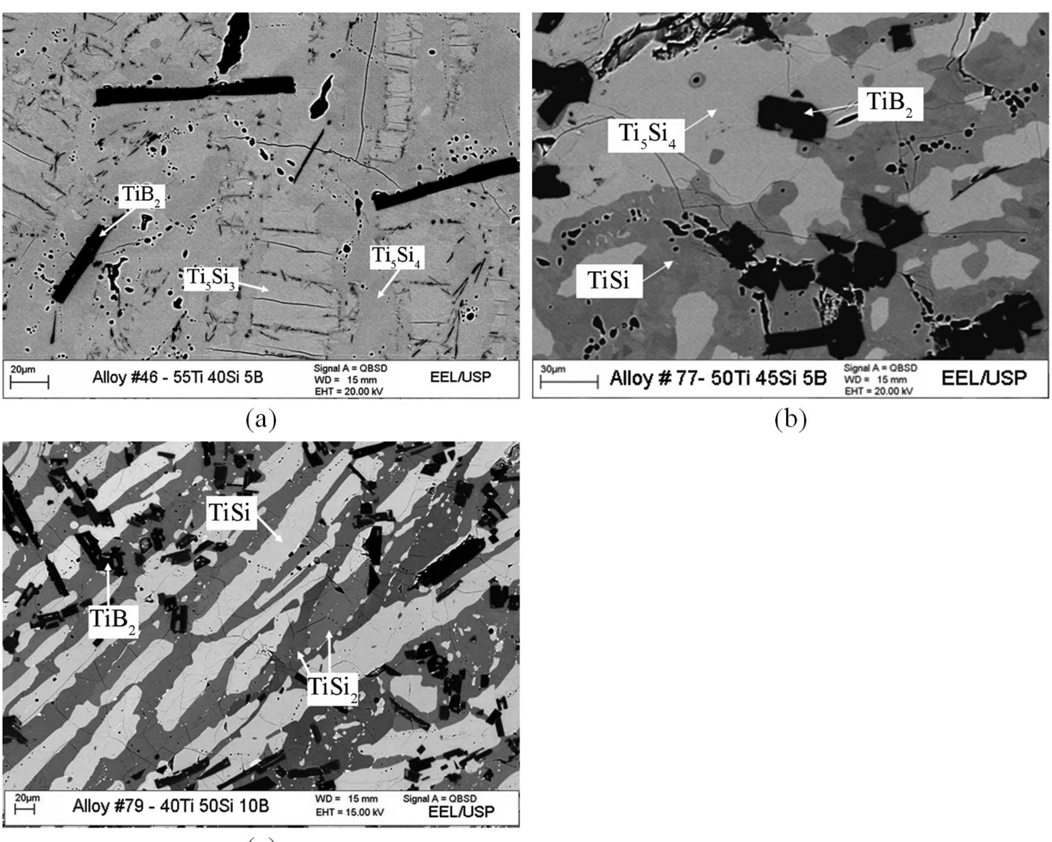


Figure 4. SEM/BSE micrographs from heat-treated Ti-Si-B alloys: (a) #46 (55Ti-40Si-5B); (b) #77 (50Ti-45Si-5B); (c) #79 (40Ti-50Si-10B).

Alloy # 79 ($Ti_{40}Si_{50}B_{10}$) revealed the presence of Ti_5Si_4, TiSi, $TiSi_2$ and TiB_2 in the as-cast and TiSi, $TiSi_2$ and TiB_2 after heat-treatment, indicating the dissolution of the Ti_5Si_4 phase. Figure 4c shows a SEM/BSE micrograph of the heat-treated sample where all the phases are present in significant amounts. The WDS data shown in Table 2 indicates the low solubility of B in both TiSi and $TiSi_2$ phases.

Alloys # 91, 92 and 93 presented TiB, Ti_5Si_3 and TiB_2 in both as-cast and heat-treated microstructures. These results indicate the difficulty to form the Ti_3B_4 from the as-cast microstructures and therefore to equilibrate these alloys in the phase fields involving this phase. Another possibility was that the Ti_3B_4 phase is not stable, in spite of its indication in the currently accepted Ti-B phase diagram. In order to check the stability of the Ti_3B_4 phase in the Ti-B system, an alloy with composition $Ti_{42.89}B_{57.11}$ (Ti_3B_4 stoichiometry) was arc-melted and heat-treated at 1250 °C for 30 days. The as-cast microstructure was formed by the phases TiB_2, Ti_3B_4, TiB and Ti_{ss}, the volume fraction of Ti_3B_4 being near 13%. The heat-treatment did not change the phases nor modify significantly amounts in the as-cast microstructure. A second as-cast sample of same composition was heat-treated at 1500 °C for 55 h and now a significant increase of Ti_3B_4 volume fraction (13% => 43%) was observed, even though thermodynamic equilibrium conditions were not reached. Spear et al.[8] have evaluated the stability of the Ti_3B_4 from annealing (1690 °C to 2070 °C for ½ to 2h) of as-cast samples with composition in the 50 to 67 at.% B range. Both XRD and SEM results showed an increase in the quantity of Ti_3B_4 phase due to annealing, indicating the stability of the Ti_3B_4 phase. Based on the results of Spear et al.[8] and our own results presented above, it is assumed that the Ti_3B_4 is also stable at 1250 °C. Thus, the existence of the $TiB+Ti_5Si_3+Ti_3B_4$ and $Ti_3B_4+Ti_5Si_3+TiB_2$ three-phase regions is proposed to be consistent with the results of alloys #69 and #46 shown previously. Furthermore, the proposed isothermal section is in agreement with those calculated by Yang et al.[5].

4. Conclusions

Phase equilibria in the Ti-$TiSi_2$-TiB_2 region of the Ti-Si-B system have been experimentally evaluated at 1250 °C from heat-treated alloys prepared via arc melting. In general, it was found to be difficult to equilibrate alloys located in the TiB-Ti_5Si_3-TiB_2 region. The ternary phase (Ti_6Si_2B) previously reported in the literature has been confirmed in this study. Very low solubility of Si in the borides as well as of B in the silicides has been noticed, thus, all the two-phase fields should be very narrow. The following three-phase equilibria have been observed: $Ti_{ss}+TiB+Ti_6Si_2B$; $Ti_{ss}+Ti_6Si_2B+Ti_5Si_3$; $Ti_5Si_3+Ti_6Si_2B+TiB$; $Ti_5Si_3+TiB+Ti_3B_4$; $Ti_5Si_3+Ti_3B_4+TiB_2$; $Ti_5Si_3+TiB_2+Ti_5Si_4$; $Ti_5Si_4+TiB_2+TiSi$; $TiSi+TiB_2+TiSi_2$.

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