THE Ti - Si INTERMETALLIC PHASES SYNTHESIS BY SHS METHOD

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Abstract

The self-propagating high temperature synthesis (SHS) was used to fabricate Ti-Si intermetallic phases. The phases were synthesized by the exothermic reaction between Ti and Si powders with proportions corresponding to the composition of Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$ phases. The XRD method was used to analyze the phase composition. The process resulted in formation of Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$ phases. A Ti_3Si phase did not occur in any produced specimens. XRD analysis showed that substrates can react with graphite mold, creating the phases containing carbon. Effect of Ti particles granulation on the phase composition was also analyzed. The results for samples fabricated by using coarse-grained Ti particles showed that this element has not reacted completely, while reducing of the granulation led to complete reaction.

Keywords: SHS method, titanium, silicon, intermetallic phases, XRD

1. INTRODUCTION

The self-propagating high temperature synthesis (SHS) is an effective method to fabricate wide range of intermetallic phases. The exothermic reaction takes place during the SHS. In the result, the temperature rises and consequently the diffusion processes lead to the synthesis of intermetallic phases. The exothermic reaction in SHS is initiated by provide of heat. The local ignition by resistive heating can be used as source of energy. The other methods involve e.g. thermal explosion ignition or laser initiation. The literature data show, that the Ti-Si intermetallic phases, particularly Ti_5Si_3, are currently commonly used in electronic, automotive and aerospace industries. They are most frequently applied as the thin layers in integrated circuits. The popularity of presented intermetallic phases is caused by their good properties, such as relatively high melting point, corrosion resistance, high hardness and Young's modulus. The disadvantages include considerable brittleness, especially at low temperatures [1-4]. The most commonly used methods of producing alloys and intermetallic phases of the Ti-Si system require the use of high vacuum, which significantly limits their fabrication and generates high costs [4, 5].

The review of world literature shows that majority of studies on Ti-Si intermetallic phases focuses on the manufacturing and testing the properties of the Ti_5Si_3 phase, characterized by highest melting point and favorable mechanical properties [6]. The research on the Ti_3Si phase shows that this phase can be produced by heat treatment of the Ti-Si alloy [7, 8] or by mechanical synthesis [5]. The literature also contains studies describing the production of the other phases from the Ti-Si phase diagram [9-12]. The Ti_5Si_3 phase is characterized by a hexagonal system. Very high melting point (2130 °C), significant hardness (11.3 GPa) and relatively high Young's modulus (225 GPa) allow the use of Ti_5Si_3 phase as a material for protective coating applied to improve hardness and resistance to oxidation at high temperatures [1]. The Ti_5Si_3 phase tends to crystallize as large crystals, significantly reduced the mechanical properties and limited the application of material. Therefore, the researchers focus on the methods allowing the production of fine-grained Ti_5Si_3 phase [2].

The papers describing the Ti_3Si phase show that it is possible to synthesize this phase by a high temperature heat treatment of Ti-Si alloy. The formation of the Ti_3Si phase requires the protective atmosphere to protect the material against negative effects of the oxygen and nitrogen from the atmosphere, which could cause a transformation of the Ti_3Si into a more stable Ti_5Si_3 phase [8]. The other study describes the production of Ti_3Si phase nanoparticles by mechanical synthesis [5]. The authors indicate the relatively good properties of this form of Ti_3Si phase.

The aim of the study was to synthesize of the intermetallic phases from the Ti-Si system by the SHS method. The process involved mixing the titanium and silicon powders with proportions corresponding to the compositions of Ti-Si phases (Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$) and SHS synthesis initiated by resistive heating. The XRD analysis was performed to identify the phase composition of synthesized samples. The effect of the grain size of titanium powder on phase composition of samples fabricated by SHS was also investigated in the study.

2. EXPERIMENTAL DETAILS

AEE TI-104 titanium powder (99.7 wt.% of Ti, particles size up to 149 µm), AEE TI-109 titanium powder (99.7 wt% of Ti, particles size up to 44 µm) and AEE silicon powder (99 wt.% of Si, particles size 1-5 µm) were used as the substrates. Coarse or fine Ti powder was mixed with Si powder, respectively. Powders were mixed in stoichiometric ratios corresponding to the composition of the Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$ phases. 10 variants of powders mixture were used (**Table 1**). The weight of each sample was 25 g.

Table 1 The variants of powders mixture

Variant	Intermetallic phase	Ti weight (g)	Si weight (g)	Ti granulation (µm)
1	Ti_3Si	20.91	4.09	149
2				44
3	Ti_5Si_3	18.49	6.51	149
4				44
5	Ti_5Si_4	17.01	7.99	149
6				44
7	TiSi	15.75	9.25	149
8				44
9	$TiSi_2$	11.50	13.50	149
10				44

Each variant of substrates was placed in sealed containers with ceramic grinding media and homogenized for 24 h. The powders mixture was then separated from the grinding media by using a sieve and placed in the reactor chamber in graphite molds. The reactor chamber was tightly closed and vented. The SHS was carried out in argon protective atmosphere at a pressure of about 0.15 MPa. The synthesis was initiated by the local ignition by transmission 220-240 A current for 30-60 s. The products were finally ground to powders by using the Abich mortar.

The quantitative phase composition of final powders was conducted on a Philips X'Pert Pro XRD device equipped with an X'Celerator band meter. The data for quantitative and qualitative phase analysis were acquired from ICCD. Quantities of the respective phases were calculated according to the Rietveld analysis [13]. The measurements were made within an accuracy of 0.5 %.

3. RESULTS AND DISCUSSION

Figure 1 shows example of the product of the self-propagating high temperature synthesis of Ti-Si intermetallic phase. The XRD patterns of the ground products for 10 variants of synthesis are shown in **Figure 2**.

Figure 1 The example of the product of self-propagating high temperature synthesis of Ti-Si intermetallic phase

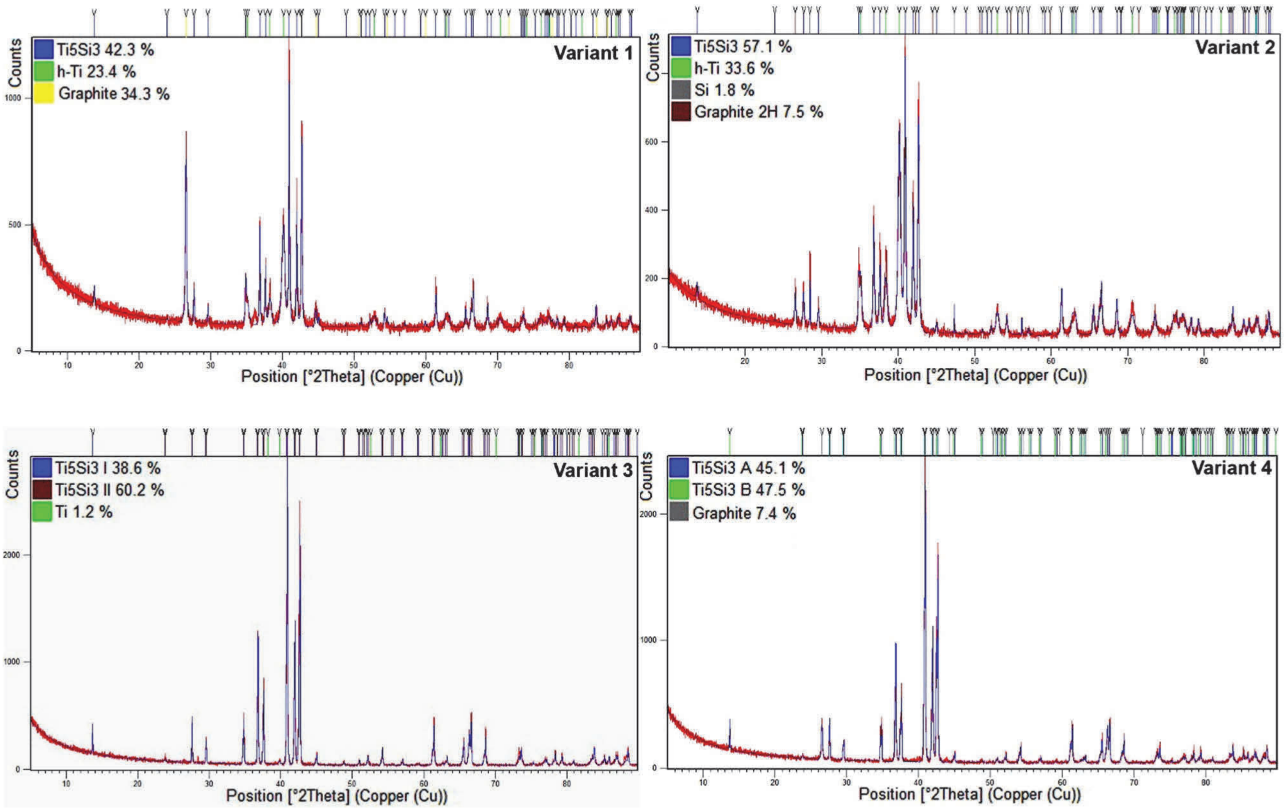

Figure 2/1 The XRD patterns of the ground products for 10 variants of synthesis

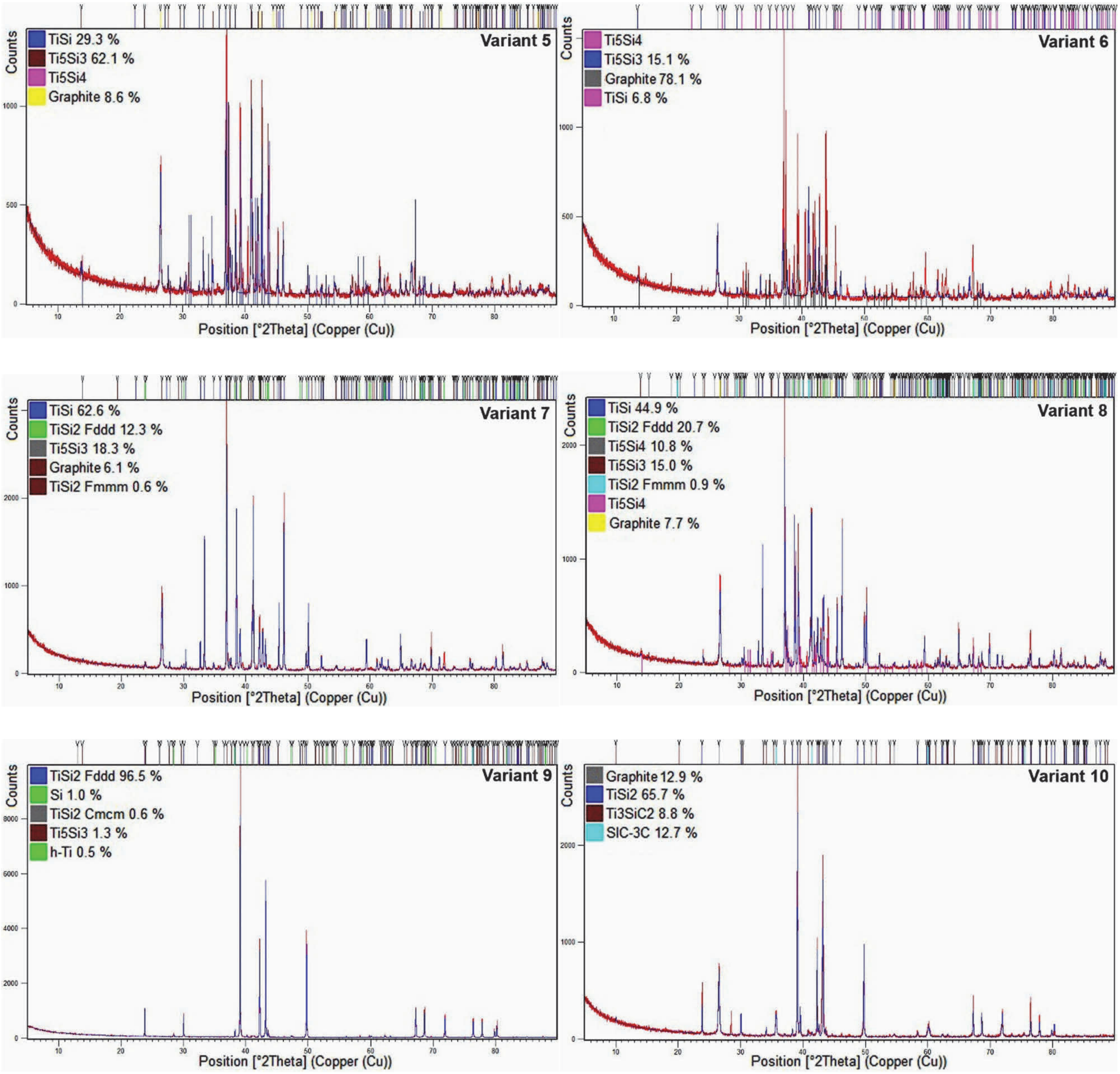

Figure 2/2 The XRD patterns of the ground products for 10 variants of synthesis

Table 2 presents the results of the quantitative XRD analysis of fabricated samples. In variant 1, Ti_3Si intermetallic phase synthesis was expected. The results of the analysis indicate that Ti_3Si did not form in this variant. The sample contains Ti_5Si_3, Ti and graphite, probably from the graphite mold in SHS reactor. Ti_3Si was also undetected in variant 2, despite Ti powder refinement. The results for variant 3 shows that designed Ti_5Si_3 phase was formed in the process. The sample likewise contained unreacted Ti. The analysis of the results from variant 4 revealed that refinement of Ti powder resulted in this case in complete reaction of Ti particles. The high content of Ti_5Si_3 phase and small contribution of the other phases in variants 3 and 4 suggests that the correct process parameters were used to synthesize Ti_5Si_3 intermetallic phase. The quantitative analysis of the results for variants 5 and 6, where Ti_5Si_4 phase was designed, was impeded by no structural pattern of this phase in the XRD database. That lack did not allow to conduct the quantitative analysis of structural constituents. The sample consists TiSi, Ti_5Si_3, graphite and the phase where no structural pattern was assigned. The results suggest that this unidentified phase is desired Ti_5Si_4 phase. The phase composition of samples for variants 7 and 8, where Ti:Si ratio was 1:1 and two various Ti powder granulation were used, shows that TiSi phase was synthesized in both cases. The contents of this phase were 62.6% and 44.9%, respectively. In addition, the other Ti-Si phases were detected in analyzed samples. The quantitative analysis for variant 9 revealed that the sample contained high content of $TiSi_2$ phase and parts of unreacted Si and Ti. Unreacted substrates did not occur in variant 10, but the analysis revealed significant content of the phases containing carbon. This results shows that graphite is not a suitable material to produce the mold to place Ti-Si samples in the SHS process.

Table 2 The results of the quantitative XRD analysis of Ti-Si phases synthesized by SHS

Variant	Projected phases	Obtained phases (at.%)						
		Ti_3Si	Ti_5Si_3	Ti_5Si_4	TiSi	$TiSi_2$	graphite	Others
1	Ti_3Si	-	42.3	-	-	-	34.3	23.4 % Ti
2		-	57.1	-	-	-	7.5	33.6 % Ti, 1.8 % Si
3	Ti_5Si_3	-	98.8	-	-	-	-	1.2 % Ti
4		-	92.6	-	-	-	7.4	-
5	Ti_5Si_4	-	62.1	detected	29.3	-	8.6	-
6		-	15.1	detected	6.8	-	78.1	-
7	TiSi	-	18.3	-	62.6	12.9	6.1	-
8		-	15.0	detected	44.9	21.6	7.7	-
9	$TiSi_2$	-	1.3	-	-	97.1	-	1.0 % Si, 0.5 % Ti
10		-	-	-	-	65.7	12.9	12.7 % SiC, 8.8 % Ti_3SiC_2

4. CONCLUSION

The Ti-Si phases were synthesized by SHS method. The process involved mixing the titanium and silicon powders with proportions corresponding to the compositions of Ti-Si phases (Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$) and the synthesis initiated by resistive heating.

The XRD analysis showed that Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$ phases were formed in the result of SHS process, while Ti_3Si phase did not occur in any produced specimens.

The substrates in a few cases reacted with graphite mold uses in the process, creating the phases containing carbon.

When coarse-grained Ti powder was used, the substrates have not reacted completely in all cases, but reducing of Ti granulation facilitated the reaction.

Satisfactory results were obtained I the case of Ti_5Si_3 and $TiSi_2$ phases, where the content of expected phase was close to 100%. In the other cases, the Ti-Si phases were also formed, but several phases were synthesized simultaneously, and the content of expected phase was smaller.

The results of the study confirmed that the SHS is an effective technique, but its noticeable disadvantage is the difficulty in controlling the process.

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