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# Effect of Fe addition on self-propagating high-temperature synthesis of $Ti_5Si_3$ in Fe–Ti–Si system

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## Abstract

The effect of Fe addition on the SHS reaction products of Fe–Ti–Si system was investigated. When Fe content is 0 wt.%, the product only consists of $Ti_5Si_3$. As the Fe content ranges from 10 to 30 wt.%, besides $Ti_5Si_3$ and Fe phases, the transient $Fe_2Ti$ is also found in the final products. With a further increasing Fe content of 40 or 50 wt.%, however, in addition to $Ti_5Si_3$, Fe and $Fe_2Ti$ phases, the FeSi phase is also detected. Furthermore, the contents of $Fe_2Ti$ and FeSi phases as well as the solubility of Fe in $Ti_5Si_3$ also increase with the increasing of Fe content. This indicates that Fe not only serves as a diluent, but also participates in the SHS reaction process. Moreover, addition of Fe has a great effect on the microstructures of SHS reaction products. When Fe content is 10 or 20 wt.%, the $Ti_5Si_3$ exhibits cobblestone-like shape. When Fe content is increased to 30 wt.%, the $Ti_5Si_3$ particulates are finer and most of them are surrounded by the bonding agents. As the Fe content is further increased to 50 wt.%, it is difficult to distinguish $Ti_5Si_3$ particulates from Fe and its compounds. The $Ti_5Si_3$ particulate sizes decrease from more than 6 to about 0.6 μm or less when Fe content in the preforms ranges from 10 to 50 wt.%. This is mainly due to the fact that the combustion temperature decreases with the increasing of Fe content. The addition of Fe provides more liquid phase for the $Ti_5Si_3$ formation during SHS reaction process. The formation mechanism of $Ti_5Si_3$ in Fe–Ti–Si system can be characterized by the solution, reaction and precipitation processes. This can be confirmed by the presence of bonding agents (remaining liquids), nearly spherical (cobblestone-like) morphology and relatively smooth surface of $Ti_5Si_3$ particulates, as well as the presence of growth striation on the surface of $Ti_5Si_3$ particulates.

*Keywords:* Intermetallics; Self-propagating high-temperature synthesis (SHS); Fe–Ti–Si; $Ti_5Si_3$; Morphology; Size; Density

## 1. Introduction

High melting point intermetallic compounds with low density, high strength and excellent oxidation resistance have received wide attention as potential aerospace materials over the past 20 years [1–5]. Among these intermetallics, the compound of $Ti_5Si_3$ has been considered as a promising material for high-temperature structural applications, in view of its high melting temperature (2403 K), low density (4.32 g/cm$^3$), high hardness (11.3 GPa), good strength at elevated temperature, excellent creep resistance, and high oxidation resistance [6–8]. However, due to its complex hexagonal structure, $Ti_5Si_3$ ($D8_8$) shows very low fracture toughness at room temperature, with low symmetry and highly covalent bonding, which increases the Peierls stress [9]. Hence, a major challenge in applying $Ti_5Si_3$-based materials, like ceramic materials, is to reduce the brittleness or improve the room-temperature fracture toughness [9].

Conventionally, $Ti_5Si_3$ has been processed by various methods, including arc melting of Ti and Si pieces [10], hot isostatic pressing or hot pressing of $Ti_5Si_3$ powders obtained by crushing the reaction sintered product [11], mechanical alloying of Ti and Si powders [12], and element powder metallurgy [13]. However, these methods are costly and have limitations on the size and purity of the product.

With the advantages of time and energy savings, self-propagating high-temperature synthesis (SHS) or known as combustion synthesis, which was developed by Merzhanov and Borovinskaya in the late 1960s [14,15], has been recognized as an alternative route to the conventional methods of producing advanced materials, including ceramics, ceramic matrix composites, intermetallics and metal matrix composites, etc. [14–18]. Due to the high heat of formation ($\Delta H^\circ_{f,298\,K} =$

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−579 kJ/mol), the SHS reaction of $Ti_5Si_3$ by Ti–Si system can be easily self-sustaining [7,15]. As a result, SHS has been routinely demonstrated as an effective and economical method of synthesis for $Ti_5Si_3$ compounds [5].

In 1990, Trambukis and Munir [19] have studied the SHS reaction of $Ti_5Si_3$ and found that the main reaction (thermal explosion) occurred in the presence of a liquid phase and was usually preceded by a relatively small reaction in the solid sate. Increasing the titanium particle size and the heating rate changed the nature of the reaction from a solid-state diffusional process to a liquid-state reaction [19]. Furthermore, also they proposed $Ti_5Si_3$ forms during SHS via a series of intermediate phases, namely $TiSi_2 \rightarrow TiSi \rightarrow Ti_5Si_4 \rightarrow Ti_5Si_3$ [19]. However, Bhaduri et al. [20] reported that the mechanism of $Ti_5Si_3$ formation was not solid–liquid or solid–solid mechanism but liquid–liquid reaction mechanism according to the thermodynamic calculations and experimental results. Recently, Yeh et al. [2,21] studied the effects of sample green density, initial sample temperature, preheating temperature, and starting stoichiometry on the combustion characteristics, as well as on the composition of final products, and they proposed the mechanism of $Ti_5Si_3$ formation was considered to be dissolution-precipitation mechanism. This was due to the fact that the combustion temperature not only was higher than the lowest eutectic temperature of the Ti–Si mixture at 1330 °C, but also exceeded the melting point of Si (1410 °C). As a result, the formation of $Ti_5Si_3$ from the stoichiometric powder compact was primarily dominated by the solid–liquid mechanism, which involves the dissolution of solid reactants into the molten liquids and the precipitation of products from the oversaturated solution [2,21]. More recently, different results were obtained by Riley [5] using a heating rate of >100 K/min and Ti particles sizes of ∼47 μm. There ultrafast in situ neutron diffraction was used to show that under certain conditions $Ti_5Si_3$ forms directly from elemental reactants ($5Ti + 3Si = Ti_5Si_3$), with no intermediate silicide phases detected [5]. The experiment suggested that a sufficiently fast rate of heating could initiate SHS combustion without significantly prior reactant inter-diffusion. Critically, the α-Ti → β-Ti transformation was identified as a significant mechanism in initiating this variety of SHS reaction [5]. This indicates that the mechanisms responsible for the SHS reaction of $Ti_5Si_3$ are still not well understood.

In addition to studying the direct reaction between Ti and Si to form $Ti_5Si_3$ as mentioned above, Yeh and Teng [22] represented a successful attempt to produce $Ti_5Si_3$–TiN composites with a wide range of compositions of 20–80 wt.% $Ti_5Si_3$ through the SHS reaction of Ti–Si system with the $Si_3Ni_4$ incorporation. However, little effort has been made to study the effect of the third metallic element incorporation on the SHS reaction of Ti–Si system.

In the present study, the effect of Fe addition on the SHS reaction of Fe–Ti–Si system is investigated. The purpose is to synthesize a large volume fraction of relatively fine and nearly spherical $Ti_5Si_3$ particulates with a certain amount of bounding agents. It is expected that the preliminary results could be significant in the promoting the development and practical application of $Ti_5Si_3$ intermetallics.

## 2. Experimental

### 2.1. Starting materials

The starting materials were made of commercial powders of 10, 20, 30, 40 and 50 wt.% Fe (99.0% purity, ∼10 μm), Ti (99.5% purity, ∼38 μm), and Si (99.5% purity, ∼15 μm), respectively. Titanium and silicon powders were used in a ratio corresponding to that of stoichiometric $Ti_5Si_3$. Powder blends with different starting compositions were mixed sufficiently by a ball milling for 6 h, and then were cold-isostatically pressed at pressures ranging from 88 to 92 MPa to form cylindrical preforms (about 20 mm in diameter and 10 mm in length) with 63 ± 2% theoretical density.

### 2.2. SHS reaction process

The SHS experiments were conducted in a combustion chamber under a protective atmosphere of industrial argon (99.9%). The preforms were placed on the graphite-flat which was fixed above a tungsten electrode and ignited by the arc heat. A small hole (2 mm in diameter and half of the preform in length) was drilled at the top of the compact, and a thermocouple pair of W–5% Re versus W–26% Re (0.5 mm in diameter) was inserted into the hole and linked up with a temperature acquisition recorder by means of which a temperature–time curve could be recorded.

### 2.3. Density and volume measurements

The theoretical density of the SHS products was calculated using the rule of mixture principle (if no volume contraction exists), while the actual density was measured using the Archimedes principle, as shown in Formulas (1) and (2), respectively.

$$\rho_t = \frac{\sum m_i}{\sum v_i} = \frac{\sum m_i}{\sum m_i/\rho_i} \tag{1}$$

$$\rho_a = \frac{m_a}{m_a - m_w}\rho_w \tag{2}$$

where $\rho_t$ and $\rho_a$ are the theoretical and actual densities; $m_a$ and $m_w$ are the mass of the samples in air and in distilled water, respectively; $\rho_w$ is the density of distilled water; $v_i$ is the theoretical volume of the SHS products. In order to reduce the error resulting from the influence of macro-porosity, the products were cut randomly from the samples with a mass of 0.2–0.4 g, which is only about 1/60–1/30 of the total mass of the SHS sample, and weighed using an electronic balance with an accuracy of 0.0001 g. The density measurements were conducted on every sample for at least five times.

Due to the inherent high porosity of the SHS products, it is difficult to measure the volume of the sample directly. As a result, the sample was used as a pattern to make a mould cavity in the plasticine, and then the liquid paraffin was cast into it to form a paraffine-sample. The volume of paraffine-sample, which has almost the same shape and volume with the SHS sample, was measured using the Archimedes principle, as shown in Formulas (3).

$$v_a = \frac{m_a - m_e}{\rho_e} \tag{3}$$

where $v_a$ is the actual volume; $m_a$ and $m_e$ are the mass of the samples in air and in ethanol (analytical pure, ≥99.7%), respectively; $\rho_e$ is the density of ethanol (0.790 g/cm$^3$).

The volume expansibility ($V_r$ or $V_p$) is calculated according to Formulas (4) and (5), respectively, as follows:

$$V_r(\%) = \frac{v_a - v_r}{v_r} \tag{4}$$

$$V_p(\%) = \frac{v_a - v_p}{v_p} \tag{5}$$

where $v_r$ and $v_p$ are the actual volume of green preform (reactant) and the theoretical volume of the SHS sample (products), respectively. The volume measurements were conducted on every sample for at least three times, and then the average values of each sample could be calculated.