

Synthesis and Reaction Mechanism of Ti₃SiC₂ by Mechanical Alloying of Elemental Ti, Si, and C Powders

Shi-Bo Li[†] and Hong-Xiang Zhai

School of Mechanical and Electronic Control Engineering, Beijing Jiaotong University, Beijing 100044, China

Formation of titanium silicon carbide (Ti_3SiC_2) by mechanical alloying (MA) of Ti, Si, and C powders at room temperature was experimentally investigated. A large amount of granules less than 5 mm in size, consisting of Ti_3SiC_2 , smaller TiC particles, and other silicides, have been obtained after ball milling for only 1.5 h. The effect of excess Si in the starting powders on the formation of Ti_3SiC_2 was studied. The formation mechanism of Ti_3SiC_2 was analyzed. It is believed that a mechanically induced self-propagating reaction is ignited during the MA process. A possible reaction mechanism was proposed to explain the formation of the final products.

I. Introduction

A NEW material titanium silicon carbide (Ti_3SiC_2) exhibits promising thermal and mechanical properties. It combines many of the best properties of both metals and ceramics, for example, it is an excellent electrical and thermal conductor, very readily machinable, relatively soft, and it has very good thermal shock and high-temperature oxidation resistance.^{1,2}

Ti₃SiC₂- or Ti₃SiC₂-based composites have been fabricated by different synthesis methods, such as chemical vapor deposition (CVD),³ arc melting,⁴ hot isostatic pressing and self-propagation high-temperature synthesis (HIP-SHS),⁵ solid-state reaction,⁶ and hot pressing (HP).^{1,7} Although Ti₃SiC₂ has been fabricated using the above methods, the sintering temperature always exceeds above 1400°C. Can Ti₃SiC₂ be obtained by using these methods only at a high temperature? This question has encouraged many researchers to find new technologies to synthesize Ti₃SiC₂. One of the most interesting technologies for obtaining ceramic compounds at room temperature is the mechanical alloying (MA) technique. This technique has attracted considerable interest in recent years. It has been used to synthesize various materials such as solid solutions, intermetallics, amorphous alloys, and ceramic composites. $^{8-10}$ Different ceramic compounds or composites were fabricated by using the MA technique. For example, MoSi2 and ZrC were synthesized by MA of elemental powders of Mo/Si and Zr/C powders, respectively.^{11,12} Shim *et al.*¹³ obtained a TiN/TiB₂ composite powder by MA of a mixture of Ti and BN. Lee *et al.*¹⁴ fabricated dense nanocrystalline TiB₂-TiC composites by field activation from high-energy ball-milled reactants. It should be noted that the MA parameters are very important in the synthesis of the above compounds or composites. Recently, a few researchers fabricated Ti₃SiC₂ by pressureless sintering of mechanical-alloyed ultrafine powders consisting of element powders of Ti, Si, and C.^{15,16}

Manuscript No. 10976. Received April 15, 2004; approved February 14, 2005. Supported by '863' program under Grant No: 2003AA332080 and BJTU Talent Foundation of China under Grant No: 2004RC005.

[†]Author to whom correspondence should be addressed. e-mail: shibo-li@sohu.com

In general, a self-propagating reaction or a combustion reaction can be triggered by MA of the alloy systems with a large negative heat of formation. The above reaction is also called a mechanically induced self-propagating reaction (MSR). The MSR reaction was first discovered by Tschakarov et al.¹⁷ during the mechanochemical synthesis of metal chalcogenides. Since then, a large number of investigations on the MSR have been performed. Different materials have been synthesized by MSR from the following systems: oxide-metal, metal-chalcogen, oxide-oxide, solid-liquid, and solid-gas reaction systems.¹⁸ The above reactions in the MSR are highly exothermic, which results in an abrupt increase in the milling vial temperature. So the ignition temperature measured from the surface of the vial is usually used to understand the mechanism of the MSR. As to Ti_3SiC_2 with a large formation of enthalpy, $H(Ti_3SiC_2)$ is -547 kJ/mol.¹⁶ Theoretically, it should be synthesized by MSR in the Ti-Si-C system.

To date, no authors have reported that the ternary compound of Ti_3SiC_2 was fabricated by MA. In this paper, the main purpose is to investigate the feasibility of the formation of Ti_3SiC_2 by MA of the elemental powders of Ti, Si, and graphite at room temperature, and to discuss the effect of Si content on the formation of the desired product.

II. Experimental Procedure

Ti (average particle size: 48 μ m, >99.2% purity, General Research Institute for Nonferrous Metals (GRINM), Beijing, China), Si (average particle size: 25 μ m, >99.9% purity, GRINM, China), and C (graphite, average particle size: 45 μ m, >99.0% purity, GRINM, China) powders were used in this experiment. The powders were mixed in dry form in mole ratios (*x* = 1, 1.3, 1.5) according to the following Eq. (1):

$$3\mathrm{Ti} + x\mathrm{Si} + 2\mathrm{C} \to \mathrm{Ti}_3\mathrm{Si}_x\mathrm{C}_2$$
 (1)

MA was carried out in a planetary ball mill (OM-1SP4) with stainless-steel milling containers and balls. The rotation speeds of the milling containers and the platform were set as 500 and 250 rpm, respectively. The milling containers with a volume of 500 mL were emptied by a pump. Three types of balls as milling medium, 400 balls of 6 mm diameter, 100 balls of 10 mm diameter, and eight balls of 20 mm diameter, were charged into each container. The weight ratio of ball to powder was 20:1. A small amount of milled powders was taken out after a selected milling time for X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observation. The vials were emptied again, and the MA was performed. XRD analysis was carried out using a D/Max-rB diffractometer (Rigaku, Tokyo, Japan) at 40 kV and 20 mA with CuKa radiation. The morphology of the powders was observed by a STEREOSCAN 360 SEM (Cambridge, U.K.) equipped with energy-dispersive spectroscopy (EDS). During the MA, the planetary ball mill was stopped at different durations in order to measure the surface temperature of containers using a thermocouple.

T. A. Parthasarathy-contributing editor



Fig. 1. X-ray diffraction patterns of the mixed powders after different milling times. The card numbers for C, Si, Ti, TiC, and Ti_3SiC_2 are #75-2078, #27-1402, #44-1294, #32-1383, and #40-1132, respectively.

III. Results and Discussion

(1) XRD Analysis and SEM Observation

Figure 1 shows the XRD patterns of Ti, Si, and C mixed powders subjected to MA at various times. Graphite's peaks disappeared from XRD patterns after only 1 h of milling, because of the formation of amorphous carbon or distribution in the grain boundaries of Ti. Both Ti and Si diffraction peaks broadened and decreased in intensity after 1 h of milling, indicating the reduction of the average crystallite size, and the buildup of defects and the formation of internal strains. After milling for 4 h, the TiC phase and the desired phase Ti₃SiC₂ with a weak reflection peak were present. The reflection peak belonging to Ti₃SiC₂ disappeared completely after milling for 8 h. This suggests that the Ti₃SiC₂ phase had been transformed to a nanocrystallite or amorphous phase. With increasing milling time, all of the TiC peaks broadened and decreased in intensity. No new phase was found, even though the milling time had been up to 60 h. The disappearance of the diffraction peak of Ti_3SiC_2 with increasing milling time suggests that the Ti₃SiC₂ phase may be formed in the range of 1-4 h. So the milled powders after milling from 1 to 3 h can be identified by XRD. The results show that Ti₃SiC₂ is formed after only 1.5 h of milling. The XRD pattern of the different powders subjected to 1.5 h milling is shown in Fig. 2, from which it can be found that the peaks of Ti₅Si₃ and



Fig. 2. X-ray diffraction pattern of the mixed powders of 3Ti-Si-2C after milling for 1.5 h. The card numbers for TiC, Ti₃SiC₂, Ti₅Si₃, and TiSi₂ are #32–1383, #40–1132, #29–1362, and #35–0785, respectively.

 $TiSi_2$ are also present, but TiC is still the main phase with larger amounts in the milled powders.

Furthermore, a large number of granules with metal brightness in the surface and less than 5 mm in size were found in inner containers after 1.5 h of milling. The appearance of these granules is shown in Fig. 3(a). Figure 3(b) shows the fracture surface of the granules. Many cavities with irregular shape were wrapped in inner granules. The granules were composed of Ti_3SiC_2 , TiC, and small amounts of silicides that were identified by XRD (see Fig. 7(a)).

The high-magnification micrograph is shown in Fig. 4(a). The product is highly porous and consists of two types of morphologies including agglomerated TiC particles (marked as arrows in Fig. 4(a)), and layered Ti3SiC2 particles accompanied by smaller TiC. Figure 4(b) shows an enlarged micrograph of the "I" area marked in Fig. 4(a), showing the particles of TiC (identified by EDS shown in Fig. 5(a)) having a round shape, smooth surface, and a size less than 2 µm. This feature indicates that TiC is formed from the reaction between Ti and C through the dissolving and precipitating mechanism in the liquid. The origin of liquid in this system will be discussed in section III(2). Figure 4(c) shows the enlarged micrograph of the "II" area, showing larger Ti₃SiC₂ particles surrounded by smaller TiC particles. Some of the smaller TiC particles were embedded in the coarse Ti₃SiC₂ grains. Many dents left on the surfaces of Ti₃SiC₂ grains were a result of debinding of the TiC. Plate-like grains with layered characteristics are typical microstructures for Ti₃SiC₂. Rodlike Ti_3SiC_2 grains (identified by EDS shown in Fig. 5(b)) were also found in the fracture surfaces (Fig. 4(d)). These features



Fig. 3. Granules formed by mechanical alloying after milling for 1.5 h shown in (a) and (b) the fracture surface of the granule.



Fig. 4. Scanning electron micrographs of the formed granules by mechanical alloying of the 3Ti-Si-2C powders after milling for 1.5 h. (a) Microstructure of the fracture surface, (b) and (c) higher magnification micrographs taken from "I" and "II" areas, respectively, marked in (a), (d) morphology of the rod-like Ti_3SiC_2 grains.

indicate that Ti_3SiC_2 had developed into two types of microstructures, with the plate-like and the rod-like forms. The above results confirm that the ternary-phase Ti_3SiC_2 can be fabricated by MA of Ti, Si, and C powders at room temperature.

It has been proved that the elemental Si tends to evaporate at elevated temperatures during sintering of Ti, Si, and C powders to fabricate Ti_3SiC_2 . This leads to a deviation from the target composition, which makes it difficult for the single-phase



Fig. 5. Energy-dispersive spectroscopy spectra from (a) smaller, round-shaped particles in Fig. 4(b), and (b) rod-like grains in Fig. 4(d) (the unmentioned peaks belong to Au).

 Ti_3SiC_2 to form. So addition of excess Si in the composition can compensate for Si loss during heat treatment.^{19,20} In the previous work, we found that excess of Si introduced in the



Fig. 6. Scanning electron micrograph of the milled powders containing smaller granules after milling of 3Ti–1.3Si–2C for 1.5 h.

Ti–Si–C mixed powders can facilitate the formation of Ti_3SiC_2 using an HP technique.²⁰ So Si with excess of 30 and 50 mol% are, respectively, added to the starting material (marked as 3Ti–1.3Si–2C and 3Ti–1.5Si–2C, respectively) for synthesis of



Fig. 7. X-ray diffraction patterns of the powders from the pulverized granules (a) 3Ti–Si–2C, (b) 3Ti–1.3Si–2C, and (c) 3Ti–1.5Si–2C.

Ti₃SiC₂ by MA. Many granules, similar to those formed in the 3Ti-Si-2C as shown in Fig. 3(a), are also found in the containers because of MA of either 3Ti-1.3Si-2C or 3Ti-1.5Si-2C after milling for 1.5 h. Figure 6 shows the micrograph of the milled powders after sifting out the larger granules; it can be observed that there are still large amounts of smaller granules with size less than 50 μ m.

The larger granules with size <5 mm formed with different contents of Si were pulverized, and then identified by XRD. The results of XRD patterns are shown in Fig. 7. It can be observed that the contents of both Ti₃SiC₂ and silicides increase with increasing Si content.

Figure 8(a) shows the fracture surface of the larger granules formed from 3Ti-1.3Si-2C. In the rich- Ti_3SiC_2 areas, smaller, round-shaped TiC particles distribute randomly. Some Ti_3SiC_2 grains with a smooth surface develop a layered morphology (Fig. 8(b)).

It should be noted that some Ti_3SiC_2 grains are also found in the TiC agglomerations as shown in Fig. 9(a), which is different from the observation in Fig. 4(b). No Ti_3SiC_2 grains can be found in the TiC agglomerations, as shown in Fig. 4(b). This indicates that the presence of more Si does favor the formation of Ti_3SiC_2 . Figure 9(b) shows a higher magnification micrograph of the marked square taken from Fig. 9(a). It can be



Fig.8. Scanning electron micrographs of the fracture surface of the granules formed after milling of 3Ti-1.3Si-2C for 1.5 h. (a) Microstructure of the Ti_3SiC_2 -rich area and (b) high magnification taken from (a).



Fig.9. Scanning electron micrographs of the fracture surface of the granules formed after milling of 3Ti-1.3Si-2C for 1.5 h. (a) Ti_3SiC_2 grains distributed in TiC-agglomerated areas, (b) higher magnification of the marked square in (a).



Fig. 10. Energy-dispersive spectroscopy spectrum from the gray phase marked in Fig. 9(a) (the unmentioned peak belongs to Au).

clearly observed that some TiC particles are enwrapped or linked by gray phases. The gray phases were identified by EDS (see Fig. 10) to be composed of about 84 at.% Ti and 16 at.% Si, indicating that the Ti–Si eutectic liquid had formed in the high-temperature system because of the occurrence of an exothermic reaction. The formation of this feature is explained in the following section.

Figure 11 shows the fracture surface of the granules formed from 3Ti–1.5Si–2C. The observation from Fig. 11(a) is different from the two former observations (as compared with Figs. 4 and 8). The fracture surface of the granules shown in Fig. 11(a) appears denser than that formed both in 3Ti–Si–2C and 3Ti–1.3Si–2C, which could be attributed to the formation of more Ti–Si phases that filled pores. From the above observations, it can be seen that the microstructure or morphology of grains in the formed granules changes as Si increases in the mixed powders.

It should be noted from Fig. 11(b) that all of the Ti_3SiC_2 grains exhibit smooth surfaces, distributing in the TiC-agglomerated areas. Figure 11(c) shows the morphology of the fracture surfaces after being treated with HF acid solution (HF:H₂O = 1:1). It can be found that Ti_3SiC_2 grains become sharp at the edges. This feature is mainly attributable to the fact that the surfaces of Ti_3SiC_2 grains are covered with a thin layer of the Ti–Si phase as Ti_3SiC_2 precipitated from the Ti–Si liquid, forming a smooth morphology. The HF solution easily dissolves silicides; therefore, Ti–Si compounds such as $TiSi_2$ and Ti_5Si_3 are leached, leaving Ti_3SiC_2 and TiC only.

(2) Reaction Mechanism for Formation of Ti_3SiC_2

As mentioned above, the MSR is easily triggered, while MA of the alloy system takes place with large exothermic heat. During the MA, the MSR may be ignited after a certain activation time, as milling reduces the particle size, thoroughly mixes the components, and increases the number of chemically active defect sites.¹⁸

In the present work, it is certain that the formation of Ti_3SiC_2 is caused by the MSR. During milling of Ti, Si, and C powders, the MSR is not ignited at the beginning of the milling process. It first undergoes a period of initial milling (incubation). During the incubation, the mixed powders are subjected to a repeated fracture and welding process. Proper pulverization results in the refinement of particles. As the milled powders are of a critical size, the diffusion distance decreases and a large surface forms, which contributes the occurrence of the ignition reaction. In the Ti–Si–C system, it is believed that a reaction between Ti and C occurs first because of the high chemical affinity of Ti to C. It is



L+ SEI BH+ (5.0 KV HD- 13 m) POTD+ 10



Fig. 11. Scanning electron micrographs of the fracture surface of the granules formed after milling of 3Ti-1.5Si-2C for 1.5 h. (a) microstructure of the fracture surface, (b) higher magnification micrograph of the TiC agglomeration area, taken from the center part of Fig. 11(a), with smooth Ti₃SiC₂ grains distributing, (c) morphology of Ti₃SiC₂ grains after treatment with HF solution.

not possible for SiC to form first, because the formation heat of TiC, $\Delta H = 185$ kJ/mol, is much larger than that of SiC, $\Delta H = 73$ kJ/mol,¹⁶ indicating that the MSR is easier to initiate in the Ti–C system than in the Si–C system with the same energy input. Furthermore, self-sustenance of a combustion reaction requires that the adiabatic temperature (T_{ad}) be at least 1800 K. For TiC, the adiabatic temperature T_{ad} is 3290 K, but that of SiC is 1860 K, which also indicates that the reaction between Ti and C for



Fig. 12. Temperature increase versus different milling times. (- -) only balls charged in the container, (- -) both balls and powders charged in the container.

formation of TiC occurs easily during the MSR. The reaction between Ti and C releases a large amount of heat, which leads to the formation of a Ti–Si eutectic liquid, because the Ti–Si system exhibits two eutectic reactions for the Si–TiSi₂ and Ti–Ti₅Si₃ compositions, both at a temperature of $1333^{\circ}C.^{21}$

The occurrence of MSR can be confirmed by the temperature rise on the surface of the containers. The temperature increase at the surface of two containers, one containing only milling balls, and the other containing the same balls and the Ti-Si-C powders, with a weight ratio of ball to powder of 20:1, is investigated. Figure 12 shows the temperature rise as a function of different milling durations. As only the milling balls are introduced into the container, the temperature rises continuously and then becomes slow after milling for 90 min. The temperature was measured to be 58°C after milling for 100 min, which is mainly because of the colliding balls and friction between the balls and the container wall. However, the temperature increase with the powders charge is higher than that of the former, as shown in Fig. 12. This indicates that the friction between the balls and powders, besides the colliding balls, produces more energy in the container before milling for 80 min. It should be noted from Fig. 12 that the surface temperature increases abruptly to 88°C after milling for 90 min, which mainly occurs because of an exothermal reaction. It is very difficult to measure the temperature of the powders directly during MA, but it can be calculated according to T_{ad} in the SHS reaction. Ye *et al.*²²



Fig. 13. Proposed mechanism of mechanically induced self-propagating reaction during mechanical alloying of the Ti–Si–C system. (a) Initial milling duration. The milled powders decrease in size and distribute to become more homogeneous, (b) C atoms diffuse along the Ti grain boundaries and remain there, forming Ti–C layers, (c) Ti–C layers are ignited with considerable heat release that leads to Ti–Si melt formation. TiC nuclei precipitate from the liquid Ti–Si, (d) Ti₃SiC₂ is formed by the reaction between TiC and Ti–Si then develops a layered morphology.

reported that the Ti–C reaction led to an increase in temperature up to 1700 K in certain regions during MA; the Al–Ti–C system in the stainless-steel container led to an increase in the surface temperature up to 70°C after being milled for 210 min. The reaction temperature in this research is estimated to be above 1700 K because of the increase in surface temperature up to 88°C. So it is possible for the Ti–Si melt to form in a higher temperature system.

Finally, in a high-temperature system, formation of the Ti–Si liquid spreads over the TiC particles, resulting in the rearrangement of particles. Ti₃SiC₂ is formed at the interfaces between the Ti–Si liquid and TiC particles as follows

$$2\text{TiC} + \text{Ti} - \text{Si} (\text{liquid}) \rightarrow \text{Ti}_3 \text{SiC}_2$$
 (2)

A possible reaction mechanism is proposed as shown in Fig. 13. At the initial MA stage, the mixed powders, consisting of two brittle components of Si and C, become fragmented and their particle sizes reduce continuously. Some fine Si and C particles are embedded into Ti particles, resulting in the refinement of the Ti particles. With increasing milling time, particle distribution tends to become more homogeneous (Fig. 13(a)). Once the particle size decreases to a critical size, large areas of grain boundaries are formed, and severe internal strain and defects are induced by MA. It is well known that grain boundaries can act as sources for dislocations. The defects and dislocations provide a rapid diffusion pathway. It is assumed that a large amount of C atoms diffuse rapidly through the pathway and accumulate in the grain boundaries of Ti, forming Ti-C layers (Fig. 13(b)). In such layers, Ti-C is only a transitional bonded state that is not the chemical TiC, but the activation energy of Ti-C for the reaction of TiC is lower than that of unmilled Ti and C powders.²³ In other words, the formation of TiC through Ti-C layers is easily induced by the impact energy of ball milling. Once the Ti-C layers are ignited, the high heat released propagates rapidly and leads to an increase in temperature in certain regions. The local temperature is high enough to induce melt Ti-Si formation; the previously formed TiC dissolves into the Ti-Si melt and nucleates from it. At the same time, several pores are also wrapped into the melt (Fig. 13(c)). In the high-temperature region, some TiC particles react with the Ti-Si liquid to form Ti₃SiC₂. Finally, Ti₃SiC₂ grains start precipitating from the melt and develop into a layered morphology. A final microstructure with high porosity is formed, as shown in Fig. 13(d). The reason why the TiC agglomerations are always found at the surface of the pores is that the capillary spreading and particle rearrangement under the liquid existing are confined near the closed pores, where the content of the Ti-Si liquid is less and some TiC fine particles grow, forming agglomerations. If the Ti-Si melt existed in the agglomerations, a reaction between TiC and Ti-Si would occur, leading to the formation of Ti₃SiC₂. This is why Ti₃SiC₂ can be found in the agglomerations with an increase in Si content in the starting powders, as shown in Figs. 9 and 11. Furthermore, some of the unreacted Ti-Si phases may be left behind (as shown in Fig. 9) while the local temperature decreases rapidly, because the MSR is very short and the heat is absorbed rapidly by the balls and containers.

Once a highly exothermic reaction takes place in a small local volume, the reaction heat will be quickly absorbed by the milling vial and balls; heat loss inhibits the formation of a self-sustaining reaction front, which cannot propagate through the entire powder mixture, and instead occurs locally at the ignition spot. So each ignited point ultimately forms a granule. This is why a large amount of granules are found in the container after the MA process is over.

In conclusion, Ti_3SiC_2 can be synthesized by MA of the elemental powders of Ti, Si, and C at room temperature. If required, pure Ti_3SiC_2 can be obtained by using the procedures reported⁶ for leaching of the pulverized granules, for example, by first using the HF solution for removing the Ti–Si compounds, and then removing TiC by heating the powders in air to 500°C and washing the oxidized powders with hot $(NH_4)_2SO_4 + H_2SO_4$ solution. Using the above-mentioned synthesis technique, pure Ti_3SiC_2 powders can be obtained, with the advantage that not only is the fabrication time shortened but also high sintering temperature is avoided and a large amount of energy is saved as compared with the reported technologies mentioned in the Introduction.

IV. Conclusions

 Ti_3SiC_2 has been synthesized by MA of Ti, Si, and C powders at room temperature after milling for only 1.5 h. With increasing Si content in the starting composition, not only did the amount of Ti_3SiC_2 rise but also its morphology changed, to become smooth. In the latter case, it is believed that Ti_3SiC_2 grains are covered with a thin layer of the Ti–Si phase as it precipitates from the Ti–Si liquid.

The main reason for the formation of Ti_3SiC_2 is that the MSR is ignited during MA of elemental powders. During the MSR process, a reaction between Ti and C is first ignited with a large amount of heat release, which induces Ti and Si to form a eutectic liquid, and then TiC dissolves into the melt and reacts with it to form Ti_3SiC_2 . Finally, Ti_3SiC_2 precipitates and develop a layered morphology. A simple reaction mechanism is proposed to explain the formation of the final product.

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