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Effect of the starting materials on the reaction synthesis of Ti_3SiC_2

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Abstract

Ternary carbide of titanium and silicon was produced via mechanical milling and following heat treatment. Effects of the starting materials, milling time and heat treatment temperature were studied. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized to evaluate the structural and morphological evolutions of the ball-milled and annealed powders. Results showed that the ball milling of TiO–Si–C as the starting materials failed to synthesize Ti_3SiC_2. Additionally, ball milling the elemental powders for shorter milling times resulted in the activation of the powders. However, after longer milling times, Ti–TiC nanocomposite was obtained. Furthermore, during annealing the milled powders, Ti_3SiC_2–TiC nanocomposite with the mean grain size of 16 nm was synthesized. After 20 h of milling, a very fine microstructure with narrow size of distribution and spheroid particles was achieved.

Keywords: A. Milling; B. Nanocomposite; D. Carbides

1. Introduction

Layered ternary carbide Ti_3SiC_2 possesses a remarkable combination of ceramic and metallic properties. It exhibits refractoriness and high-temperature properties normally associated with ceramics, alongside the electrical and thermal conductivity of metals [1–3]. In addition, Ti_3SiC_2 exhibits ductility due to the layered structure, which enables it to be readily machinable with ordinary cutting tools [4]. Other mechanical properties of Ti_3SiC_2 include excellent thermal shock resistance, reasonable fracture toughness, high Young's modulus and good high-temperature strength [5–8].

There are many synthesis methods adopted to formulate Ti_3SiC_2 such as chemical vapor deposition (CVD) [9,10], arc-melting [11], hot isostatic pressing and self-propagation high-temperature synthesis (HIP-SHS) [12,13], solid-state reaction [14], hot pressing (HP) [15–17], reaction sintering [18] and plasma sintering [19–21].

Lately, mechanically activated synthesizing (MAS) process, including mechanical milling of the mixed powder to obtain a superfine structure (1st step) followed by heat treatment (2nd step), has drawn much attention, due to its capability to synthesize various homogeneous and nanostructure materials. Mechanical alloying (MA) is basically a dry and high-energy ball milling technique used to synthesize alloys, oxide-dispersion-strengthened alloys, amorphous alloys and various intermetallics compounds [22,23].

Liang et al. produced high purity Ti_3SiC_2 ceramic using MA and spark plasma sintering (SPS) and investigated the effect of trace amount of Al on the processes [24]. Riley et al. and Li et al. investigated the influence of high-energy ball milling on the self-propagating high-temperature synthesis (SHS) of titanium silicon carbide (Ti_3SiC_2). The milled powders comprised TiC, Ti_3SiC_2 and silicides because a mechanically induced self-propagating reaction (MSR) was triggered during mechanical alloying [25,26].

In this work Ti_3SiC_2 was synthesized via mechanical alloying and heat treatment using two kinds of starting materials. Moreover, attempt was made to reduce the milling time and heat treatment temperature in order for the rapid synthesis of Ti_3SiC_2.

2. Experimental

The starting materials consisted of Ti (99.9%, <100 nm), Si (99.8%, <200 nm), C (99.9%, <50 nm) and TiO (99%,

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<300 nm). The powders were mixed in the stoichiometric ratio based on the following reactions:

$$TiO + Si + C = Ti_3SiC_2 + CO(or CO_2 or SiO_2) \quad (1)$$

$$3Ti + Si + 2C = Ti_3SiC_2 \quad (2)$$

In the first reaction, the practicality of TiO reduction by Al or C was investigated and in the second reaction the feasibility of the direct reduction of elemental powders was studied. The milling experiments were executed in a planetary ball mill using a stainless steel cup (125 ml) with the ball to powder weight ratio (BPR) of 15:1. High chromium stainless steel balls were used in argon atmosphere with the pressure of 4 atm. The speeds of the cup and the main disk were 525 and 275 rpm, respectively. To analyze the samples, they were removed in a glove box by interrupting the ball mill at various time intervals.

X-ray diffraction (XRD) analysis was applied using Philips (30 kV and 25 mA) diffractometer with Cu Kα radiation (λ = 1.5404 Å) for phase transformation and crystallite size evolution during milling and heat treatment. The XRD trials were performed with the step size and time per step of 0.02 degrees and 1 s, respectively. The morphology of the mechanically alloyed powders was studied by means of Philips scanning electron microscope (SEM) operating at 20 kV. To investigate the thermal behavior of the milled powders, conventional heating in an atmosphere controlled tube furnace was used. Heat treatment was executed at the temperatures of 600 and 1100 °C with the heating rate of 15 °C/min under argon flow atmosphere.

3. Results and discussion

3.1. TiO reduction

In the first method, the practicability of TiO reduction for the synthesis of Ti_3SiC_2 was studied. Silicon and graphite were used as the reducing agents. The structural evolutions of the starting materials during milling are illustrated in Fig. 1. Milling led to the decrease of the integrated intensity of the silicon and graphite peaks after 5 h and at longer time period of milling (15 h) all of the reducing agent peaks (Si and C) disappeared. These results indicate that the disappearance of Si and C may be due to: (1) intimate mixing of the starting materials and the absorption of the diffracted X-rays of light atomic weight atoms by high atomic weight ones and (2) solid solution formation. The first possibility can be disregarded attributable to the approximately same mass absorption coefficient of the starting materials (TiO and Si) [27]. On the other hand, it is correct for the disappearance of the carbon peaks. The second possibility can be confirmed by the shift of the solvent phase peaks due to the embedding of the solute atoms in the lattice of the solvent phase. It can be seen in Fig. 1 that the TiO peaks as solvent phase, shifted to higher angles that signifies the formation of TiO (Si) solid solution and the smaller size of the Si atom. With increasing the milling time to 20 and 50 h, solid solution formation continued (shift of TiO peaks) and all of the Si solved in the TiO lattice. At the end of milling, the nanocrystalline solid solution of TiO (Si) formed with the mean grain size of 19 nm. This measurement was based on the XRD profile analysis by Scherrer formula with the details presented in our previous paper [28].

Two kinds of samples were annealed. In the first 3 h-milled sample, solid solution formation process was in the initial stage and in the second 50 h-milled sample, this process accomplished. Fig. 2 reveals the results of these heat treatments. All of the peaks are known as TiO. The heat treatment caused the sharpening of the TiO peaks that is due to the microstructure refinement (grain growth and strain releasing). On the other hand, the mean grain size of TiO (50 h milled) increased from 19 nm to 25 nm during annealing.

3.2. Direct reaction of the elemental powders

Elemental powders of silicon, graphite and titanium were mixed in the stoichiometry of Ti_3SiC_2. Fig. 3 shows the XRD patterns of these starting materials. The structural evolutions of the milled powders are shown in Fig. 4. In the early stage of milling, only the broadening of the Ti peaks and strong decrease in the Si and C peak intensities took place. Lack of any shift in the Ti peak positions leads to the conclusion that no reciprocal

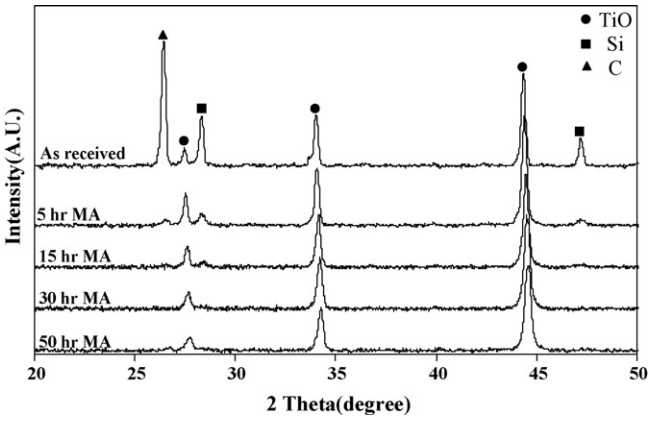

Fig. 1. Effect of the milling on the reaction synthesis of Ti_3SiC_2 by XRD diffraction (route 1).

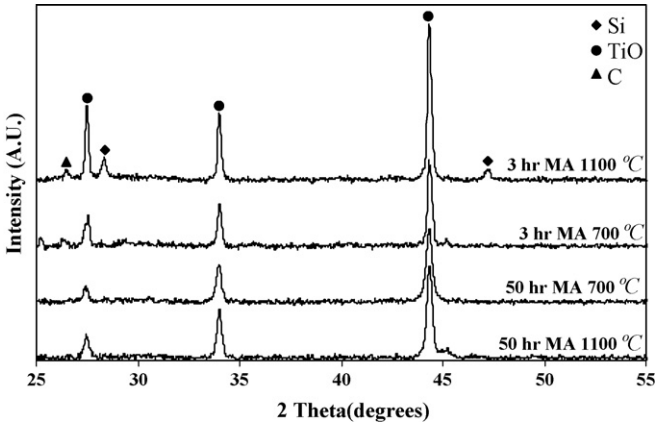

Fig. 2. Effect of the annealing on the reduction of TiO for the synthesis of Ti_3SiC_2 (route 1).

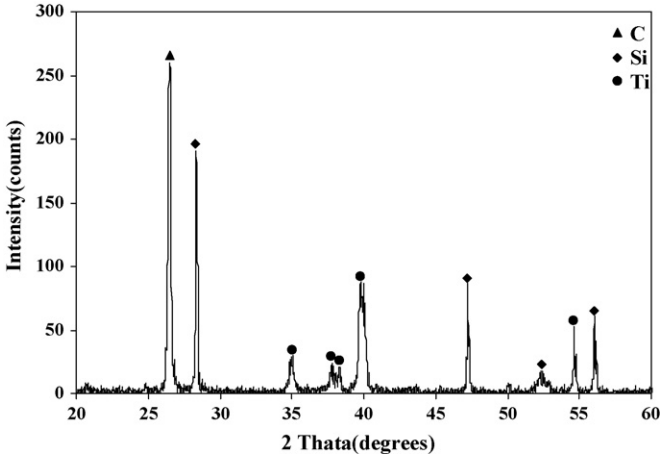

Fig. 3. XRD pattern of the as received materials in the direction reaction method (route 2).

solid solution has occurred. It seems that the process of intimate mixing in the early stages of milling is responsible, to a large extent, for the decrease in the intensity of the Si and C reflections. In fact, the Si and C diffractions diminished significantly due to the high X-ray absorption coefficient of Ti [27].

The initial mixing continued up to 12 h of milling and initiated the formation of nanocrystalline amorphous like structure. This is confirmed by the greatly broadened peaks of Ti after 12 h of milling. Due to this extra broadening of the Ti peaks, the measurement of the mean grain size and lattice strain by conventional Scherrer and Williamson–Hall methods [23] is impossible. As milling continued for 30 h, the TiC peaks appeared in the pattern, meanwhile, the Ti peaks with the decreased intensity can still be observed. The formation of TiC instead of Ti_3SiC_2 implies that the former is thermodynamically and kinetically favorable i.e. the Gibbs free energy formation of the former is more negative than the latter [29]. With further milling to 45 h, the Ti peaks disappeared and the TiC peaks broadened. Disappearance of the Ti peaks is due to the very fine microstructure of the powders. In other words, Ti exists in the composition but its peaks cannot be observed because of the higher mass absorption coefficient of TiC than Ti.

The results of the milling showed that the synthesis of Ti_3SiC_2 via milling only is impracticable, so the milled powders were annealed at different temperatures of 700 and 1100 °C. The milled samples can be categorized in two groups: (1) the powders that were only mechanically activated and no new phase was synthesized and (2) the powders at higher milling time that included Ti and TiC. The results of the heat treatment are presented in Fig. 5. Annealing the 6 h-milled sample at 700 °C did not affect the starting composition considerably i.e. the raw materials peaks (Ti, Si and C) can still be seen in the pattern. Meanwhile, the very small peaks of Ti_3SiC_2 and TiC appeared in the pattern. Also the other effect of this annealing is the sharpening of the peaks of the starting materials, due to the grain growth and strain releasing. In spite of this microstructure refinement, the mean grain size of Ti increased from 8.5 nm (in 20 h-milled sample) to 37 nm.

As annealing temperature rose to 1100 °C, a large amount of the starting materials transformed to Ti_3SiC_2 and TiC and the

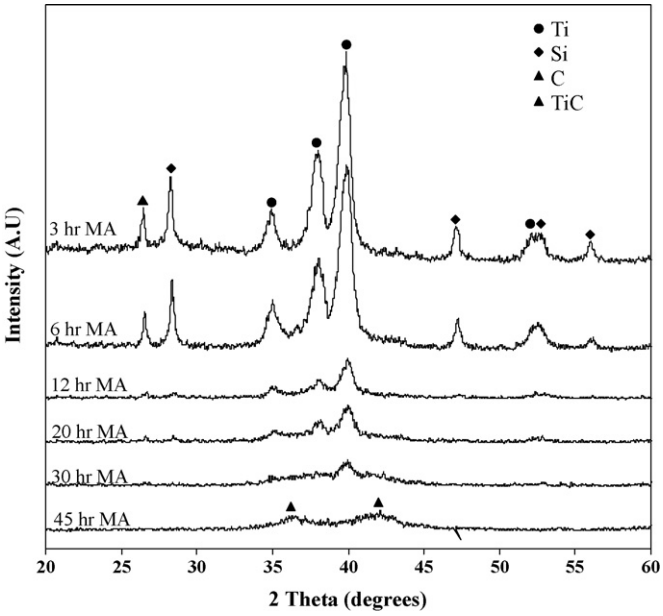

Fig. 4. X-ray diffraction patterns of ball-milled powders for different time periods (route 2).

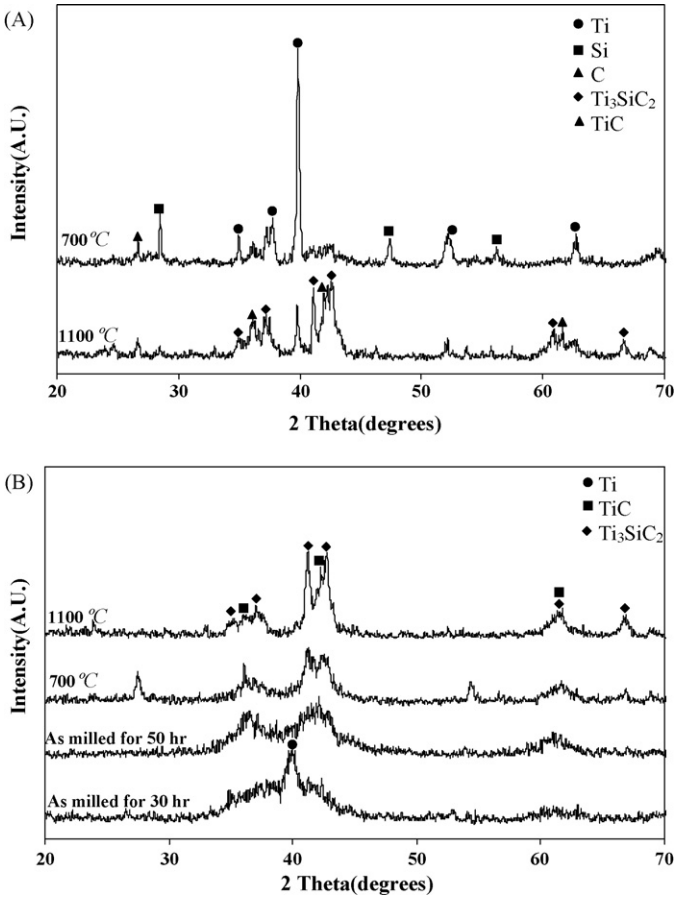

Fig. 5. Structural evolution during the annealing of mechanically alloyed powders detected by X-ray diffraction: (a) 6 h and (b) 50 h milled (route 2).

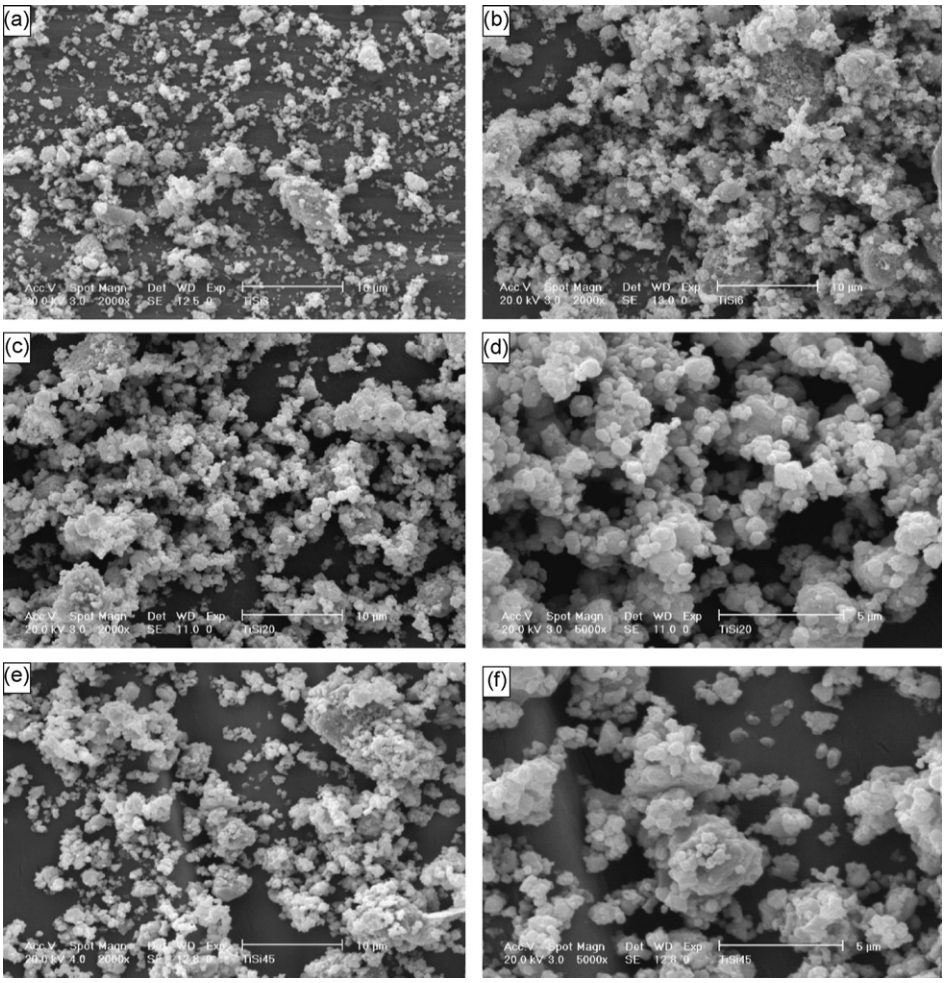

Fig. 6. Morphology of ball-milled powders by SEM; (a) 3 h, (b) 6 h, (c) 20 h, (d) 20 h milled at higher magnification showing a superfine and homogenous morphology, (e) 45 h and (f) 45 h milled at higher magnification showing agglomeration phenomenon at the end of milling (route 2).

nanocomposite of Ti–Ti_3SiC_2–TiC was obtained. Due to the overlapping and low intensity of these phases, the measurement of the mean grain size and lattice strain was impossible.

The heat treatment of the 50 h-milled powder had the same results as the previous. The annealing led to the formation of the TiC–Ti_3SiC_2 nanocomposite but it should be noted that the TiC and Ti_3SiC_2 were synthesized during milling and annealing, respectively. The consequence of this phenomenon was the very good distribution and mixing of these phases that resulted in the improvement of mechanical properties. The mean grain size of Ti_3SiC_2 was 16 nm that confirms the formation of the TiC–Ti_3SiC_2 nanocomposite. It can be concluded that we can prepare TiC–Ti_3SiC_2 composite by means of annealing.

For the investigation of the morphological changes during milling, the scanning electron microscopy was used. It can be seen in Fig. 6(a) that the particles had very uneven and irregular shape and size. These differences in the early stage of milling are due to the dissimilarity of the starting materials which were mixed. Ductility of the metallic powders caused heavy plastic deformation and agglomeration during milling. This is obvious in Fig. 6(b) that plastic deformation of the Si and Ti led to adhering and agglomeration of the smaller particles after 6 h of milling. The agglomeration and cold welding were the dominating phenomena at this stage of milling. With increasing the milling time to 20 h, the role of cold welding decreased. In contrast, the effect of work hardening and fracturing increased. We can see this evolution in Fig. 6(c) that the cold-welded particles in the previous stage fractured and formed the smaller particles and agglomerates. On the other hand, there is equilibrium between cold welding and work hardening. This equilibrium led to the formation of very similar particles with very narrow size distribution and spheroid shape. The other effect of this process was the decrease in the average particles size, which is obvious in Fig. 6(d). Fig. 6(e) shows the morphology of the powder at the end of milling. It is apparent that the small particles of previous stage of milling agglomerated again and formed a very uneven and irregular distribution as in the 3 h-milled sample. Fig. 6(f) shows this process clearly at higher magnification.

4. Conclusion

The feasibility of Ti_3SiC_2 synthesis via mechanical alloying and following heat treatment was investigated. Two kinds of starting materials were used. Reduction of TiO as a source of Ti could not be performed during milling and annealing. Direct

reaction of the elemental powders was impossible during milling. In the shorter milling time, the starting materials only activated and at the longer milling time, the Ti–TiC nanocomposite was obtained. The heat treatment of the milled powders led to the formation of the Ti_3SiC_2–TiC nanocomposite. The SEM analysis showed a very fine microstructure with narrow size distribution of spheroid particles after 20 h of milling.

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