Synthesis of Ti_3SiC_2 by high energy ball milling and reactive sintering from Ti, Si, and C elements

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ABSTRACT

We present an original method of preparation of nanostructured Ti_3SiC_2 compound based on high energy ball milling and reactive sintering techniques. Starting materials are Ti, Si, and C elements. X-ray diffraction and secondary electron microscopy are used to identify the formed phases and to analyze the obtained microstructures. Lower milling intensity and shorter milling time are found as the best milling conditions in order to get an intimate mixture of the three elements without formation of detectable secondary phases. The optimized sintering temperature is equal to 1350 °C. A method used for minimizing the oxygen content in the final compound is presented.

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1. Introduction

Ti_3SiC_2 compound was wildly investigated recently as a member of nanolayered machinable ceramics [1,2]. It owns unusual combination of metallic and ceramic properties due to the special nanolayered atomic structure, such as high thermal and electrical conductivities, low density, and excellent oxidation resistance below 1100 °C, high modulus and exceptional damage tolerance. These properties could make Ti_3SiC_2 as a potential nuclear material [3] whether the brittle to ductile transition (DBT) could be drastically reduced. Nanostructuration could be a promising way to meet this requirement. Even many processes were employed to fabricate Ti_3SiC_2, such as hot-isostatic pressing (HIP), hot pressing (HP), self-propagation high-temperature sintering (SHS), spark plasma sintering (SPS) or pulse discharge sintering (PDS), it was difficult to get nanostructured Ti_3SiC_2. Recently, more and more attention was paid on high energy ball milling or mechanical alloying to fabricate Ti_3SiC_2 because using highly deformed and reactive powders could reduce sintering temperature and holding time [4–7]. By the way, Li et al. synthesized Ti_3SiC_2 powder with the purity of 95.8 vol.% by mechanical alloying 3Ti/Si/2C powder mixture for 10 h, and subsequent vacuum heat-treating at 1000 °C for 1 h [4], then they fabricated dense Ti_3SiC_2 by pressureless sintering of mechanical alloyed element powder with purity close to 80% and relative density 99% [5]. Orther et al. got a single-phase of Ti_3SiC_2 by sintering for 2 h a ball-milled powders mixture consisting of 3Ti/1.3Si/2C at 1350 °C [6]. Liang et al. obtained Ti_3SiC_2 with

relative density 98.9% and purity 99.3 wt% by mechanical alloying 3Ti/Si/0.2Al/2C powder mixture for 10 h and then sintering by SPS at 1100 °C for 5 min with heating rate 100 °C/min and 30 MPa pressure [7]. In this work, high energy ball milling and reactive sintering techniques were chosen in order to get in a first step a pure Ti_3SiC_2 compound. The next step will consist to get nanostructured and fully dense material via rapid hot pressing.

2. Experimental

Ti (93–95%, 40 μm), Si (99.5%, 44 μm), graphite (99.997%, 75 μm) powders and Si bar (99.5%) were used in this study. The nominal composition was set to 3Ti/1.2Si/2C. These raw materials were weighted and then milled in an instrumented vibrating frame grinder (Pulverisette 0 FRITSCH) [8]. The device consists of a tungsten carbide vial and a tungsten carbide ball, the mass of which is 1000 g. The raw materials were prepared in a glove box under argon and then the vial was evacuated (10^{-5} Torr) prior to milling. Milling time and milling intensity are two major parameters for vibrating frame grinder. The milling times were 24, 72, and 120 h, respectively. The 'milling intensity' was defined as the momentum transferred by the ball to the unit mass of powder per unit time [8] according to the following equation:

$$I = M_b V_b f / M_p \ (\mathrm{m/s^2}),$$

where M_b and V_b are respectively the mass and velocity of the ball when hitting the powder and f is the frequency of collisions of the ball with the powder. In present work, the milling intensities were 1300, 2360, and 2710 m/s^2, respectively.

Differential thermal analysis (SETARAM, TAG 24) equipment was used as the reactive sintering furnace for the time being. Phase

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identification was carried out by X-ray diffraction (Panalytical, using Co $k_{\alpha1}$ radiation), and the microstructure was observed by scanning electron microscopy (Zeiss). The quantitative element analysis was examined by electron microprobe (Cameca SX50).

3. Results and discussion

Whatever the milling conditions are, the ball-milled powder is made of nanosized particles of Ti and Si as deduced from XRD experiments, whereas the diffraction peak of graphite disappear. However, for a very high milling intensity, new diffraction peaks appear which are the signature of titanium carbide. It is well known that TiC exists as a secondary phase in bulk Ti_3SiC_2 prepared by various methods [1,9,10] and is deleterious to high-temperature oxidation resistance [11]. But Yang and co-workers have shown many times that TiC also acts as a starting material for Ti_3SiC_2 synthesis [12–16]. In this research, we have selected the ball milling conditions that avoid TiC formation in course of milling due first to minimize the pollution coming from the milling media and second to ensure the complete formation of the ternary carbide during sintering, TiC particles being not beneficial to the subsequent reactive sintering. Fig. 1 gives an overview of the milling conditions which are detrimental to our approach.

In order to assess the effect of milling conditions, we chose two milling conditions 24 h–2360 m/s^2 (without TiC formation) and 120 h–2710 m/s^2 (with TiC formation) and examined their phase evolution during heating at different temperature. For 24 h and 2360 m/s^2 (Fig. 2(a)), only two phases, Ti and Si were detected after ball milling in XRD pattern, the peaks belonging to graphite disappeared due to the formation of amorphous phase [17]. At 450 °C (not shown here for brief), the as-milled powder just released the strain and recovered. A new phase TiC formed until 650 °C and $Ti_5Si_3C_x$ came out at 850 °C. Then TiC and $Ti_5Si_3C_x$ became two major phases at 1050 °C, and only a small amount of desired Ti_3SiC_2 phase was formed at this temperature. At 1350 °C, Ti_3SiC_2 increased dramatically with simultaneous consumption of TiC and $Ti_5Si_3C_x$, $TiSi_2$ appeared first time at this temperature. With the temperature increasing again, Ti_3SiC_2 decomposed into TiC and $TiSi_2$. So, for the milling condition 24 h–2360 m/s^2, the best sintering temperature is 1350 °C. Comparing the phase revolution of 24 h–2360 m/s^2 and Zhang et al. [18], we conclude that the appearing temperature of TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2 is lower than that of Zhang, This is the effect of high energy ball milling as previous research showed [4–7].
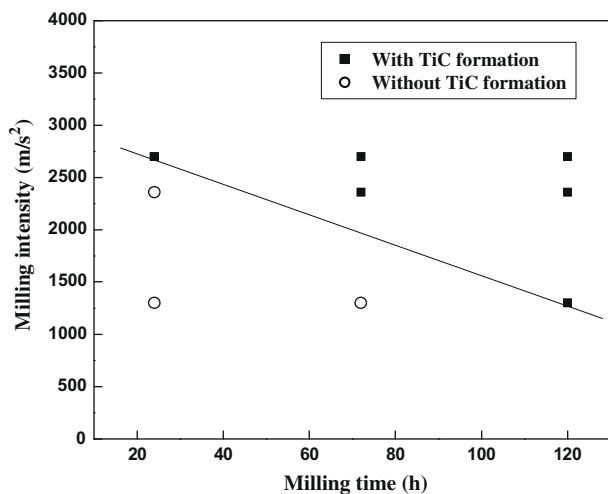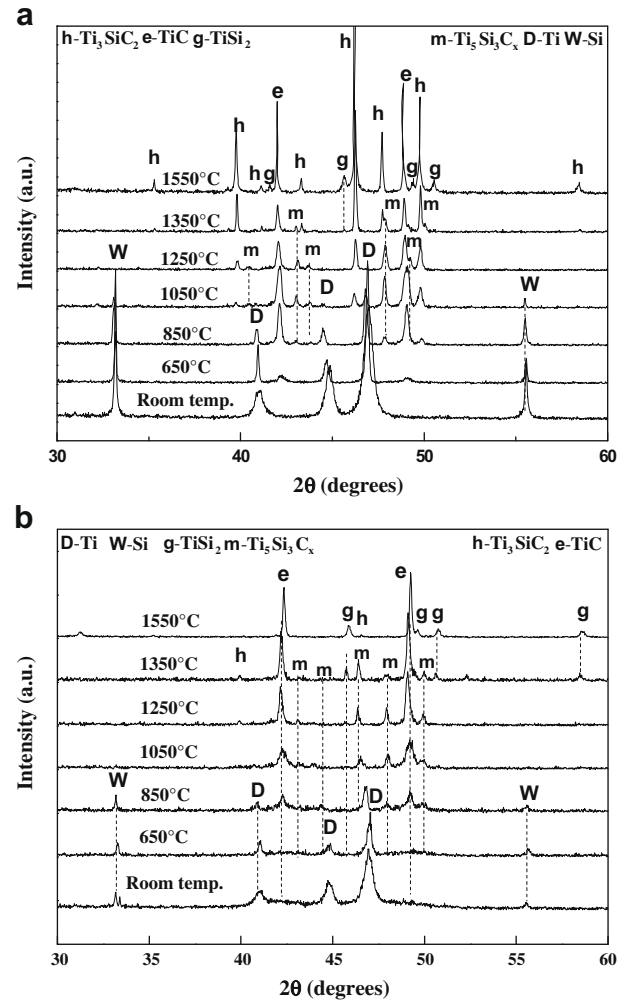

Fig. 2. Phase evolutions of different milling conditions at various temperatures: (a) 24 h–2360 m/s^2 and (b) 120 h–2710 m/s^2.

We also investigated the phase evolution of 120 h–2710 m/s^2 (Fig. 2(b)). The difference between 120 h–2710 m/s^2 and 24 h–2360 m/s^2 is described as follows: firstly, TiC phase already formed after ball milling and existed as a major phase from 1050 °C to 1550 °C in 120 h–2710 m/s^2 because the high energy condition.
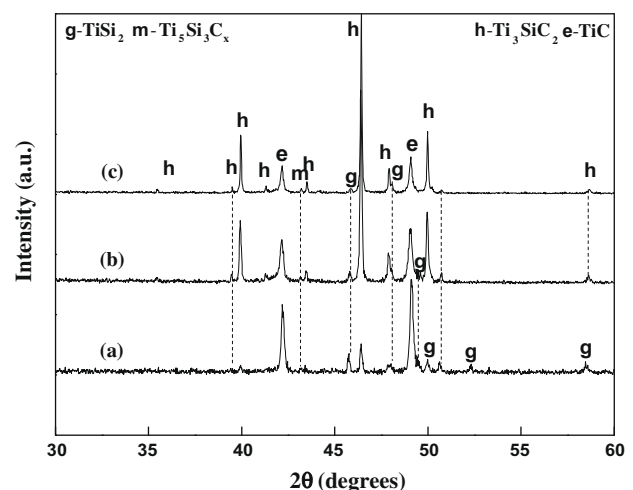

Fig. 1. Influence of the milling intensity and milling time on the TiC formation after ball milling.

Fig. 3. X-ray diffraction patterns of: (a) three elements powder; (b) Ti, graphite powder and Si bar and (c) Ti powder, Si bar and degassed graphite.

Secondly, only small amount of Ti_3SiC_2 was found from 1050 °C to 1350 °C but decomposed at 1550 °C.

According to these experiments, 24 h–2360 m/s^2 and 1350 °C were chosen as the best milling conditions and holding temperature. As discussed above, avoiding TiC formation was one reason that we chose lower milling intensity and shorter milling time, nevertheless, we also checked again that purity of starting compounds, especially oxygen content that is difficult to estimate on raw powders, was another important factor for high energy ball milling [19]. The oxygen should come from the raw material but not during the process because we always prepared the powder in the glove box, and then the vial was evacuated prior to milling. Thus, in order to remove the oxygen, we used Si bar instead of Si powder and then we degas graphite at 1000 °C for 12 h in vacuum. The reactive sintering results of three samples which were prepared at 1350 °C with 3Ti/1.2Si/2C were demonstrated in Fig. 3: (a) Ti, Si, and graphite element powders; (b) Ti, graphite powders and Si bar; and (c) Ti powder, Si bar and degassed graphite. We could see that Ti_3SiC_2 content increased dramatically when we replaced Si powder by Si bar, then we used Si bar and degassed graphite simultaneously, the Ti_3SiC_2 content increased further.

4. Conclusion

We sintered Ti_3SiC_2 by Ti/1.2Si/2C elements at 1350 °C after ball milling 24 h with a milling intensity equal to 2360 m/s^2. We also investigated the effect of the purity of the raw powder on the sintering results by substituting Si and graphite powders with Si bar and degassed graphite. The further work is going on in order to get fully dense materials and pure Ti_3SiC_2 via rapid hot pressing.

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