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Rapid fabrication of Ti_3SiC_2–SiC nanocomposite using the spark plasma sintering-reactive synthesis (SPS-RS) method

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A mixture of Ti, C, Si powders and Al (as a sintering aid) was adopted to synthesize the Ti_3SiC_2–SiC nanocomposite using the spark plasma sintering-reactive synthesis method. SiC did not form directly from Si and C, but from intermediate phases TiC_x and $Ti_5Si_3C_y$, leaving C. The grain size of Ti_3SiC_2 is about 5 μm, but the average grain size of SiC is about 100 nm. With its fine microstructure, the Ti_3SiC_2–20 vol.%SiC composite shows improved mechanical properties at room temperature.

Keywords: SPS; Nanocomposite; Reactive synthesis; Ti_3SiC_2/SiC

Ti_3SiC_2 is a useful material as it combines the merits of metals and ceramics [1,2]. Like metals, it has good electrical and thermal conductivities, damage tolerance, good machinability and resistance to thermal shock. Like ceramics, it has high specific stiffness. The potential applications of this material are myriad and are far from being exhausted. For example, it can be used as a structural material for high-temperature applications, machinable ceramics, kiln furniture, heat exchangers and bioinert ceramics, and for applications where rotating parts are used [1]. However, because of its low hardness and machinability, Ti_3SiC_2 is not wear resistant. In addition, at high temperatures, above 1000 °C, its oxidation resistance is not very good [8].

It is well known that SiC has promising mechanical properties in hardness, wear resistance and oxidation resistance, and SiC is thermodynamically stable with Ti_3SiC_2 [3,4]. Therefore, the fabrication of Ti_3SiC_2–SiC composites has attracted much attention, and it has been verified that Ti_3SiC_2–SiC composites exhibit improved hardness, wear and oxidation resistance [5–11]. Many attempts to synthesize Ti_3SiC_2–SiC composites have been carried out by hot pressing (HP) or hot isostatic pressing (HP) methods. These methods require a high sintering temperature and a long sintering time. In addition, the SiC grain sizes of the obtained samples are mostly comparable to or even bigger than those of the Ti_3SiC_2 matrix. It has been validated that coarse SiC inclusions are detrimental to the tensile properties [8]. Coarse SiC inclusions would induce the residual tensile stresses in the matrix, and then cause flexural strength degradation [11]. Thus, the attempt to fabricate Ti_3SiC_2–SiC composites with finer SiC reinforcing particles is an obvious fruitful area for further research.

In recent years, spark plasma sintering (SPS) has been used as a rapid sintering method for ceramic materials [12]. SPS is a newly developed sintering technology that can lower the sintering temperature and decrease the sintering time greatly. In our previous work, in situ synthesis and sintering of submicron TiC–SiC composites, Ti_5Si_3–TiC, Ti_5Si_3–TiC–Ti_3SiC_2 and TiN–Al_2O_3 nanocomposites using the SPS technique were successfully carried out [13–16]. Most importantly, we reported an extremely simple one-step method, that is, the spark plasma sintering-reactive synthesis (SPS-RS)method, to produce pure, dense nanocomposites using sub-micron starting powders. This novel fabrication process for nanocomposites basically involves molecular-level mixing of raw powders during the reaction process instead of conventional powder mixing. The as-prepared nanocomposites have finer microstructures and exhibit high mechanical properties.

Based on the above research, the main objective of this work was to prepare Ti_3SiC_2–SiC nanocomposite using the SPS-RS method from elemental powders of Ti/Si/C. In order to erase the impurity of TiC, Al was used as sintering aids. The reaction path of Ti_3SiC_2–SiC

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nanocomposites was studied to benefit understanding of the formation mechanism of SiC nanophase.

The raw materials used in this work were 99% pure Ti powder (10 μm), 99.9% pure C powder (1.6 μm), 99% pure Si powder (2 μm) and 99% pure Al powder (45 μm). Ti, C and Si powders were mixed with a small amount of Al powder (lower than 1 wt.% in the mixed powders) to yield a SiC content of 20 vol.% in the end-product. After being mixed and dried, the mixtures were sintered by an SPS apparatus (SPS-2040, Sumitomo Coal Mining Co., Tokyo, Japan) in vacuum (less than 6 Pa). The employed heating rate was 100–200 °C/min, the applied pressure was 70 MPa and the holding time was about 6 min at different sintering temperatures before turning off the power.

The as-sintered samples were ground and analyzed by X-ray diffraction (XRD). Archimedes' method was adopted to identify the degree of densification. After being polished, the microstructure analyses of the samples were conducted using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Vickers hardness (H_v) of the polished samples was measured by the indentation technique (Wilson-wolpert Tukon® 2100B). The indentation parameters were made using a 10 kg load with a dwell of 15 s. Some samples were machined and polished to 2 mm × 3 mm × 18 mm bars for measuring the three-point bending strength with a span of 12 mm. Six measurement runs were carried out to determine the average value.

Figure 1 shows the X-ray diffraction patterns of Ti_3SiC_2–SiC composites sintered at different temperatures, as well as the raw powder mixtures. As the amount of Al is too little to be identified by XRD, only the peaks of Ti, Si, and C are presented in the powder mixtures. For the samples heated at 900 °C, TiC_x and $Ti_5Si_3C_y$ phases were newly formed, with some remaining Ti, Si and C, indicating the rapid occurrence of two reactions, namely

$$Ti + xC \rightarrow TiC_x \tag{1}$$

$$5Ti + 3Si + yC \rightarrow Ti_5Si_3C_y \tag{2}$$

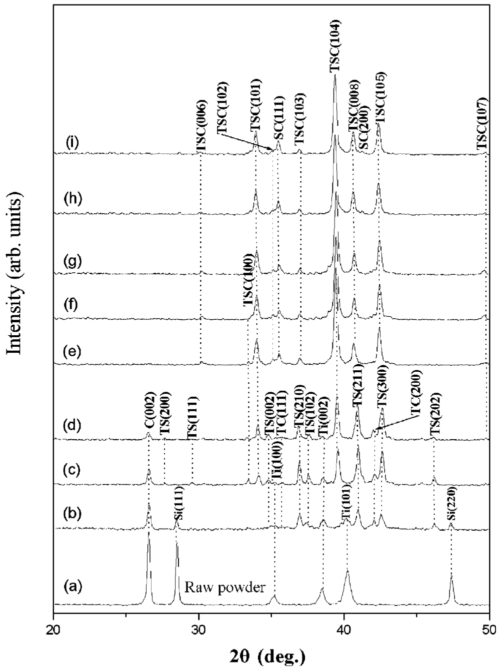

Figure 1. XRD patterns of the Ti/Si/C mixed powders heated at (b) 900, (c) 1000, (d) 1100, (e) 1150, (f) 1200, (g) 1250, (h) 1280 and (i) 1300 °C (TSC = Ti_3SiC_2; TC = TiC_x; TS = $Ti_5Si_3C_y$; SC = SiC).

In the Ti–Si system, there are five intermetallic compounds, Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$. Among them, Ti_5Si_3 is the most thermodynamically stable phase, with the most negative formation enthalpy ($\Delta H = -579$ kJ/mol) [17]. Therefore, Ti_5Si_3 was formed primarily by the reaction between Ti and Si. The $Ti_5Si_3C_y$ phase can be considered as a solid solution of carbon into the binary silicide Ti_5Si_3, and the effect of the doped C on the variation in the lattice constants of Ti_5Si_3 is quite small [18–20]. Recent work has shown that small additions of carbon can enhance the stability of the $D8_8$ structure, because the formation enthalpy becomes more negative [18]. In this work, the formation of TiC_x and $Ti_5Si_3C_y$ is explored on the basis of free energy changes for the possible reaction for TiC and Ti_5Si_3. For comparison, the Gibbs free energy curve of reactions (1), (2), (4) and (5) was presented in Figure 2 for TiC (or TiC_x) Ti_5Si_3 (or $Ti_5Si_3C_y$), Ti_3SiC_2 and SiC [2,21,22].It can be seen that the Gibbs free energy of Ti_5Si_3 and TiC formation is more negative than that of SiC, thereby favoring the formation of Ti_5Si_3 and TiC on a thermodynamic basis instead of SiC. Although the Gibbs free energy of Ti_3SiC_2 formation is more negative than that of TiC, Ti possesses high chemical affinity to C. Therefore, some Ti and C atoms will react to form TiC before Ti_3SiC_2. It has been reported that Ti_5Si_3, TiC and Si can react to form Ti_3SiC_2 [23], as shown in reaction (3), which leads to the appearance of some Ti_3SiC_2 at 1100 °C

$$Ti_5Si_3 + 10TiC + 2Si \rightarrow 5Ti_3SiC_2 \tag{3}$$

In the temperature range of 900–1100 °C, the peaks of Ti, Si and C decrease gradually. It can be identified that Si peaks disappear at 1100 °C, but SiC peaks appear at 1150 °C, which indicates that Si does not react directly with C to form SiC. The reason for the disappearance of Si peaks is that reaction (3) takes place. Tan et al. simply described the formation of Ti_3SiC_2–SiC composite from Ti, Si, C powders as follows [11]:

$$3Ti + Si + 2C \rightarrow Ti_3SiC_2 \tag{4}$$

$$Si + C \rightarrow SiC \tag{5}$$

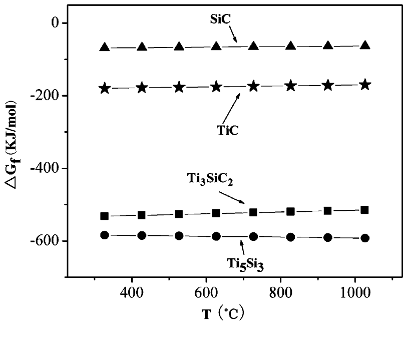

Figure 2. The Gibbs free energy curve of reactions (1), (2), (4) and (5) as a function of temperature.