Microstructure Characterization and Mechanical Properties of TiSi₂–SiC–Ti₃SiC₂ Composites Prepared by Spark Plasma Sintering

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Dense TiSi₂–SiC and Ti₃SiC₂–SiC–TiSiC₂ composites in which SiC particles in 200–300 nm disperse, were reactively synthesized through spark plasma sintering (SPS) technique using TiC, Si, and C powders in micrometer as starting reactants. The phase constituents and microstructures of the samples were analyzed by X-ray diffraction, field emission scanning electron microscopy and transmission emission spark plasma sintering (SPS) technique using TiC, Si, and C powders in micrometer as starting reactants. The phase constituents and microstructures of the samples were analyzed by X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy (TEM) equipped with energy-dispersive spectroscopy (EDS) were employed to examine the microstructure. The hardness and fracture toughness of the samples reach 5.4 ± 0.3 MPa m¹/² and 700 ± 50 MPa, respectively. The factors leading to the improvement of the mechanical properties were discussed.

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1. Introduction

In last ten years, advanced material systems for high temperature application based on refractory intermetallic compounds have been extensively investigated.¹,² Among various classes of these intermetallic systems, titanium silicides have been identified as potential high temperature structural materials due to their superior combination of high melting point, oxidation resistance, and mechanical and microstructural stability. TiSi₂ is one of the most important titanium silicides. Besides the properties mentioned above, it has relatively high thermal and electrical conductivities that make it candidate for diffusion barriers and electronic interconnection applications.³) The relatively low hardness makes the material easy to be machined. However, as in the case of many intermetallic compounds, the application of TiSi₂ compound is still greatly restricted by the low fracture toughness (about 2.2 MPa m¹/² for pure TiSi₂) and low bending strength (about 170 MPa for pure TiSi₂).⁴) A promising alternative method is to produce a TiSi₂ matrix composite.

In Ti–Si–C system, there are many important compounds. SiC is a good candidate for reinforcement because it has high hardness, good high temperature strength and oxidation resistance. Li et al. synthesized TiSi₂–SiC composites by hot pressing Ti, Si and TiC powders with an enhancement of mechanical properties as compared to pure TiSi₂.⁵) Nowadays Ti₃SiC₂ received much attention because of its unique combination of metallic and ceramic properties, such as good electrical conductivity, relatively high fracture toughness, good oxidation resistance and high temperature strength.⁶,⁷) These properties ensure it suitable as the reinforcement component in ceramic-based composite.⁸,⁹) Wang et al. synthesized Ti₅Si₅–TiC–Ti₃SiC₂ nanocomposite in which TiC and Ti₃SiC₂ were the dispersive phases for reinforcements.¹⁰) However, TiC doesn’t possess good high temperature oxidation resistance, which will decrease the high temperature oxidation resistance and strength of the composites. SiC is good substitute of TiC because of its good high temperature strength and oxidation resistance. So it is interesting to fabricate SiC and Ti₃SiC₂ reinforced TiSi₂–SiC–Ti₃SiC₂ composites.

Spark plasma sintering (SPS) technique is a new process with the advantages of rapid heating speed and short sintering time. Especially the short sintering period is advantageous in suppressing exaggerated grain growth. SPS has been used for fabricating a lot of kinds of ceramics, metal and biomaterials, such as Al₂O₃, Ti₃SiC₂, TiC–SiC, TiNi and hydroxyapatite.¹¹–¹⁵) In this work, TiSi₂–SiC and Ti₃SiC₂–SiC–Ti₃SiC₂ composites were in situ synthesized by spark plasma sintering to strengthen the TiSi₂.

2. Experimental Procedure

Commercially available C, Si and TiC were used as the starting powders. The mean particle sizes of C, Si and TiC were 9, 75 and 1.47 μm, respectively. The Si:TiC:C molar ratios of 6:2:0 and 6:4:1 were chosen as the starting compositions, marked as composition 1 and composition 2, respectively. They were blended in ethanol in Planet Ball Milling Machine for 12 h with agate media. After drying at 70 °C for 12 h, the blended powders were screened through a 200-mesh sieve. Then the samples were sintered in a SPS apparatus (Sumitomo Coal Mining Co., Tokyo, Japan) under uniaxial pressure of 60 MPa in vacuum (below 6 Pa). The heating rate was controlled in the range of 150–200 °C min⁻¹. The sintering temperature was held at 1000, 1100, 1200 and 1260 °C respectively for dwelling 5 min.

The densities of the resultant samples were measured according to the Archimedes’s method. The crystalline phases were characterized by X-ray diffractometer (Rigaku: D/max 2200PC) with CuKα radiation. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) equipped with energy-dispersive spectroscopy (EDS) were employed to examine the microstructure. The hardness and fracture toughness of the samples

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were measured at room temperature by the Vickers diamond indentation method under a load of 49 N and a dwell of 10 s. The fracture toughness \((K_{IC})\) values were calculated using the following expression:\(^{16}\)

\[
K_{IC} = \frac{P(b)}{(2\sqrt{\pi})^{3/2} \tan \beta} \cdot b^{-1},
\]

where \(P\) is the Vickers load, \(b\) is the average length of cracks, and \(\beta\) is 68°. Three-point bending tests were performed to determine the strength using an Instron-5566 type of universal testing machine. The samples used in the bending tests were rectangular bars of 3 × 2 × 18 mm. The speed of crosshead displacement was 0.5 mm min\(^{-1}\) with the span of 12 mm.

3. Results and Discussions

3.1 Microstructure

Figures 1(a) and (b) are the X-ray diffraction patterns of the starting powder and the resultant product of composition 1, respectively. Figure 1(b) shows that the sample consisted of TiSi\(_2\) as a major phase coexisting with SiC phase without other phases, indicating that TiSi\(_2\)–SiC composite could be in-situ fabricated by spark plasma sintering according to following reaction [eq. (1)]:

\[
3\text{Si} + \text{TiC} \rightarrow \text{TiSi}_2 + \text{SiC} \quad (1)
\]

However, TiSi\(_2\)–SiC–Ti\(_3\)SiC\(_2\) composite could not be fabricated only by using Si and TiC as reactants even the sintering temperature was as high as to 1260°C. C powder was added to the starting powders of Si and TiC. Figure 2 shows the X-ray diffraction patterns of the samples of composition 2 sintered at different temperatures. After sintered at 1000°C for 5 min, the constituents of the sample are the same with those of the starting powder indicating that reaction didn’t begin at 1000°C. After sintered at 1100°C for 5 min, the diffraction peaks of Si disappeared and those of both TiSi\(_2\) and SiC appeared. At the same time, the intensity of diffraction peaks of C and TiC became weak, indicating that reaction between Si and TiC occurred at this temperature. Fig. 2(d) is the diffraction spectrum of the sample sintered at 1250°C with dwelling time of 5 min. The diffraction peaks of TiSi\(_2\) existed except those of TiSi\(_2\) and SiC. It indicated that part of TiSi\(_2\) reacted with TiC and C to form Ti\(_3\)SiC\(_2\) as eq. (2):

\[
\text{TiSi}_2 + 2\text{TiC} + \text{C} \rightarrow \text{Ti}_3\text{SiC}_2 + \text{SiC} \quad (2)
\]

From these results, it can be concluded that the ternary composites should be formed through a two-step reaction process. Firstly, Si reacts with TiC at about 1100°C, and then part of TiSi\(_2\) reacts with TiC and C to form Ti\(_3\)SiC\(_2\) above 1100°C.

And the whole reaction should be [eq. (3)]:

\[
6\text{Si} + 4\text{TiC} + \text{C} \rightarrow \text{TiSi}_2 + 3\text{SiC} + \text{Ti}_3\text{SiC}_2 \quad (3)
\]

Figures 3(a) and (b) show the backscattered SEM images of polished surfaces of composition 1 and composition 2, respectively. The SiC particles (dark area) distributed uniformly in the composite. The dark spots in Fig. 3 were the SiC-rich areas rather than single SiC crystals. The white area is the mixture of TiSi\(_2\) and Ti\(_3\)SiC\(_2\) in Fig. 3(b). It is difficult to distinguish Ti\(_3\)SiC\(_2\) from TiSi\(_2\) only by the back scattered image.

Figure 4 shows the TEM images of grains of TiSi\(_2\)–SiC [Fig. 4(a)] and TiSi\(_2\)–SiC–Ti\(_3\)SiC\(_2\) [Fig. 4(b)] samples. In Fig. 4(a), the SiC grains with grain size of 200–300 nm mainly disperse on the TiSi\(_2\) grain boundaries. A lot of strain stripes emerge in Fig. 4(a) because of the thermal mismatching between TiSi\(_2\) and SiC. There are some Ti\(_3\)SiC\(_2\) plates confirmed by electron diffraction in composition 2 as shown in Fig. 4(b). The length of Ti\(_3\)SiC\(_2\) grain is more than 1 μm and every Ti\(_3\)SiC\(_2\) grain contains several layers. Ti\(_3\)SiC\(_2\) grains have dominant (0001) facets because they grow most easily along the directions present within the basal plane. So Ti\(_3\)SiC\(_2\) usually has a layered crystalline structure and the morphology of grains appears to be plate.

3.2 Mechanical properties

The hardness, fracture toughness and bending strength values listed in Table 1 are the average data of 6 tests. The
Fracture toughness values of Ti$_2$Si–SiC and Ti$_2$Si–SiC–Ti$_3$SiC reach 3.3 ± 0.2 MPa m$^{1/2}$ and 5.4 ± 0.3 MPa m$^{1/2}$, which are 150 and 250% higher than that of monolithic Ti$_2$Si (2.2 MPa m$^{1/2}$).

The improvement in fracture toughness for Ti$_2$Si–SiC and Ti$_2$Si–SiC–Ti$_3$SiC composites was possibly attributed to the combination of crack deflection and crack bridging mechanisms. When the crack meets the dispersed SiC particles, it deflects and part of it propagates through the SiC particles. As we know, Young’s modulus, thermal expansion coefficient and chemical compatibility of the matrix and second phase particles affect the properties of the composite. Because the thermal expansion coefficient of Ti$_2$Si (σ$_{TiSi2}$ = 10 × 10$^{-6}$ K$^{-1}$) is larger than that of SiC (σ$_{SiC}$ = 4.8 × 10$^{-6}$ K$^{-1}$), hydrostatic compressive stress appears in the second phase (SiC). At the same time, there will be radial compressive stress and tangential tensile stress in the matrix around the SiC particles. If the SiC locates on the crack extension plane, the crack will firstly reach the boundary of the Ti$_2$Si and SiC grains. The surface energy of SiC grains is much larger than the interface fracture energy of Ti$_2$Si/SiC interface. So the crack tends to bypass the SiC particles and propagate along the Ti$_2$Si/SiC interface. However, sometimes the crack drills through the particles if the particles are irregular. As the TEM image shows, the size of the SiC is in the range of 200–300 nm, so the effect of the crack deflection on the improvement of fracture toughness was weakened. When the crack extension direction is not parallel to the priority growth direction of Ti$_3$SiC$_2$, the crack will propagate along the interface between matrix and Ti$_3$SiC$_2$. Because the length of the Ti$_3$SiC$_2$ grain is more than 1 μm, the effect of the crack bridging on the improvement of fracture toughness is remarkable. Figure 5 is the back scattered images of typical trajectories of indentation crack extension of composition 2.
In the course of the crack propagation in Fig. 5(a), crack branching, crack bridging and crack deflection can be observed at the same time. At some points, the crack propagated in a zigzag fashion or deflected at a vertical angle. Crack deflection of this degree is very rare in common ceramic. It can be found clearly that the layered Ti$_3$SiC$_2$ grain was pulled out from the TiSi$_2$ matrix in Fig. 5(b). The crack bridging of Ti$_3$SiC$_2$ mainly contributed to the improvement of the fracture toughness of TiSi$_2$–SiC–Ti$_3$SiC$_2$.

The bending strength values of TiSi$_2$–SiC and TiSi$_2$–SiC–Ti$_3$SiC$_2$ composite reach 450 ± 50 and 700 ± 60 MPa, which are much higher than that of monolithic TiSi$_2$ (170 MPa). Figure 3 shows that the microstructure of TiSi$_2$–SiC–Ti$_3$SiC$_2$ is finer than that of TiSi$_2$–SiC composite, which in some extent led to the enhancement of the bending strength. Besides grain size, grain shape could affect the strength of materials as well. It was believed that better contact or joint could form between the long grains, which could improve the fracture strength of grains. Wang et al. utilized rodlike β-Si$_3$N$_4$ crystal to strengthen MoSi$_2$ matrix and effectively improved the flexural strength and fracture toughness. In bending tests, the crack propagation experienced a course which was similar with the crack spread in indentation tests. So the crack bridge aroused by layered Ti$_3$SiC$_2$ also contributed to the improvement of bending strength.

4. Conclusion

In this work, TiSi$_2$–SiC–Ti$_3$SiC$_2$ composites were successfully in-situ fabricated using TiC, Si and C particles in micrometer as starting reactants. The microstructure characterization results showed that in-situ synthesized SiC grains with grain size of 200–300 nm mainly dispersed on the TiSi$_2$ grain boundaries. The fracture toughness has been shown to increase from 3.3 ± 0.2 MPa-m$^{1/2}$ for TiSi$_2$–SiC composite up to 5.4 ± 0.3 MPa-m$^{1/2}$ for the TiSi$_2$–SiC–Ti$_3$SiC$_2$ composite. And the bending strength was improved from 450 ± 50 MPa up to 700 ± 60 MPa. The improvement in fracture toughness was attributed to crack deflection and crack bridging resulted from nano-SiC particles and layered structural Ti$_3$SiC$_2$ grains. The introduction of layered Ti$_3$SiC$_2$ also improved the bending strength of the composites greatly.

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REFERENCES