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Fabrication and fracture analysis of $MoSi_2$ matrix composites by mechanical alloying①

MA Ying(马 颖)[1], HAO Yuan(郝 远)[1], ZHANG De-liang(张德良)[2], YU Ning(余 宁)[1]
(1. School of Materials Science & Engineering, Gansu University of Technology, Lanzhou 730050, P. R. China;
2. Department of Materials and Process Engineering, University of Waikoto, Hamilton 3150, New Zealand)

[Abstract] Four composites, $MoSi_2$+ ZrO_2, $MoSi_2$+ $ZrO_2(Y_2O_3)$, $MoSi_2$+ ZrO_2+ SiC and $MoSi_2$+ $ZrO_2(Y_2O_3)$ + SiC are fabricated by mechanical alloying. It is clear that cracks produced on the $MoSi_2$ matrix composites during hardness testing belong to the Palmquist crack system. The value of highest fracture toughness of $MoSi_2$+ ZrO_2+ SiC composite is 7.58 MPa•$m^{1/2}$, which is nearly three times that of monolithic $MoSi_2$. This can be attributed to well-distributed ZrO_2 and SiC particles along the boundaries of very fine $MoSi_2$ grains.

[Key words] mechanical alloying; composites; fracture toughness; $MoSi_2$; ZrO_2; Y_2O_3
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1 INTRODUCTION

$MoSi_2$ is one of the intermetallic compounds which have the potential in being used as advanced high temperature materials[1]. It has high melting point (2030 ℃), high ductile/brittleness transition temperature (1000 ℃), high oxidation temperature (1600 ℃), relatively low density (6.30 g/cm^3) and low heat expansion efficient (10^{-6}/K). The raw materials for producing $MoSi_2$ are low cost materials. However, $MoSi_2$ has its disadvantages, which include high production cost due to the high melting point, and inherent brittleness and low strength at high temperature. Producing $MoSi_2$ by using a combination of mechanical alloying and powder consolidation processes has a potential advantage in lowering the cost substantially, since the processing temperature is significantly lowered. To improve high temperature strength and fracture toughness, $MoSi_2$ matrix composites reinforced with ceramic particles such as ZrO_2 and SiC are developed[2]. Mechanical alloying is a superior process to produce such composites[3~7]. Therefore, the $MoSi_2$ and its composites are fabricated by using mechanical alloying in this paper. The results of a study on fracture toughness of $MoSi_2$ matrix composites reinforced with ZrO_2 and SiC particles are described.

2 EXPERIMENTAL

The mechanical alloying (MA) was carried out with a planetary grinding machine. The Mo, Si and SiC powder were used with more than 99.9% in purity and approximately 5 μm in average particle size. Two types of ZrO_2 powder were used: one containing 2.5% Y_2O_3 (mole fraction), while the other being monolithic. The particle size of ZrO_2 was in the range of 15~ 20 nm. Suitable amounts of Mo, Si, ZrO_2 and SiC powder were mixed and then sealed together with a number of stainless steel balls in a stainless steel pot under an argon atmosphere. The diameters of the steel balls were 10 mm and 20 mm respectively, and the mass ratio of balls to powder was 15∶1. The rotation speed of the grinding machine was 200 r/min. Samples were taken out at regular time intervals for X-ray diffraction (XRD) analysis. The mechanically alloyed composite powder was hot pressed into d 50 mm × 12 mm cylinders at 1700 ℃ using 35 MPa pressure. Each of the samples was hot pressed for 30 min. The hot pressing was done under an argon atmosphere by using a high strength graphite mould. After hot pressing, the furnace was slowly cooled to 1400 ℃, and the sample was taken out to polish into mirror surface along the vertical direction of pressure. Then the cylinders were cut into a number of 40 mm × 4 mm × 3 mm rectangular test samples for three point bending tests and metallgraphic examination.

3 RESULTS AND DISCUSSION

3.1 Fabrication of $MoSi_2$ matrix composites by MA

Within the first 30 h of mechanical alloying, it is found that the intensity of both Mo and Si peaks in the XRD patterns decreases. It appears that the intensity of Si peaks decreases more rapidly than that of

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Mo peaks. Similar observation during mechanical alloying of Mo and Si was also reported previously[8]. After milling for 163 h, the Si peaks disappear completely, and very wide $MoSi_2$ peaks appear, as shown in Fig. 1. The XRD pattern is similar to that obtained by Kim et al[9]. It can be seen from Fig. 1 that the addition of ZrO_2 does not influence the fabrication of $MoSi_2$.

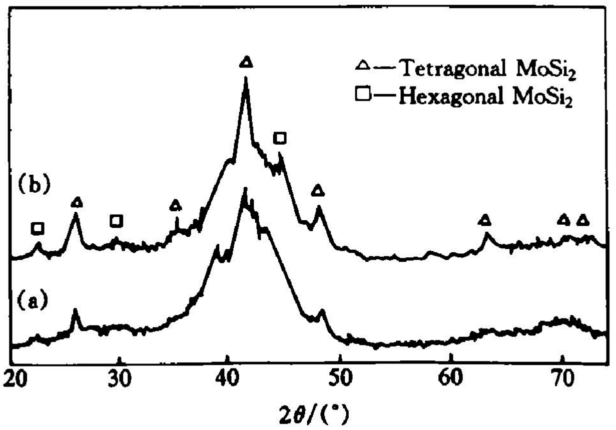

Fig. 1 XRD patterns of powders mechanically alloyed for 163 h
(a) —Mo-Si-ZrO_2 powder; (b) —Mo-Si powder

Fig. 2 shows the particle morphology of the powder mixture of Mo, Si and ZrO_2 milled for 300 h. Equiaxial shape particles can be seen and the average diameter of the particles is approximately 1 μm.

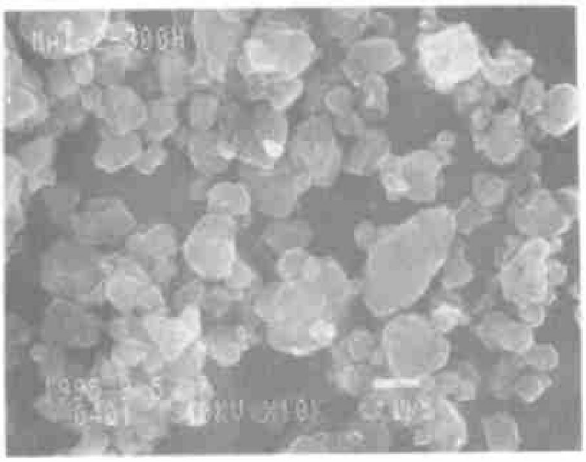

Fig. 2 Morphology of Mo-Si-ZrO_2 powder after milling for 300 h

Fig. 3 shows the change of grain size of $MoSi_2$ as a function of milling time. The grain size was estimated by using the Scherrer's equation[10]. It can be seen from Fig. 3 that the grain size of $MoSi_2$ decreases significantly during the early period of milling. In the middle stage of milling, the decrease rate of grain size becomes significantly smaller. In the last stage of milling (after milling for 210 h), the grain size of $MoSi_2$ remains almost unchanged with increasing milling time. The minimum grain size of $MoSi_2$ achieved is approximately 8 nm in diameter.

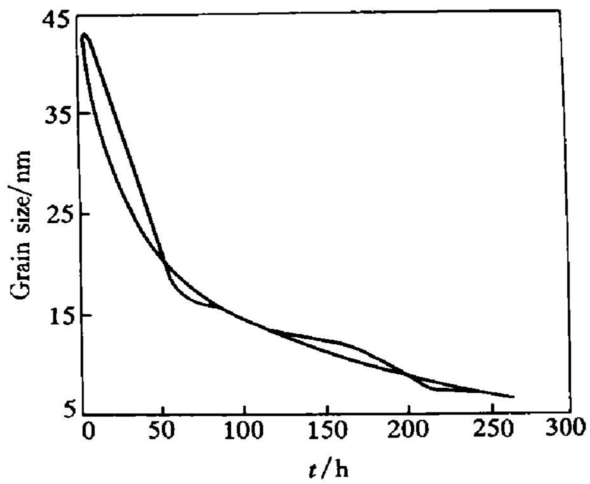

Fig. 3 Change of grain size of $MoSi_2$ as function of milling time

3.2 Fracture toughness

Indentation method is usually used to determine the fracture toughness of $MoSi_2$ indirectly. When measuring the Vickers hardness of a brittle material, two kinds fo cracks can be produced as a result of the indentation: Median crack and Palmquist crack. The different cracks are due to different sensitivities of the material to the applied stress field under the diamond indenter. When Median cracks are produced, the material has the low fracture toughness; when Palmquist cracks are produced, the material has a much better fracture toughness. Median cracks start from the corners of an indent both before and after polishing. Palmquist cracks appear to start from the corners of an indent before polishing, but appear to start from points that are some distance away from the corners of an indent after polishing.

It is believed that the cracks produced on $MoSi_2$ and its composites are Median cracks, and accordingly, Anstis equation is used to calculate the value of K_{IC}[11].

$$K_{IC} = 0.016(E/H)^{0.5} P \cdot c^{-1.5} \quad (1)$$

where E is elastic modulus, H is hardness, P is pressure and c is lattice parameter.

Fig. 4 shows the crack morphologies of the four $MoSi_2$ matrix composites fabricated in this experiment before and after polishing respectively. It can be seen that the indents have clear and complete edge. Before polishing, cracks start from the corners of indents, and then become curved. Therefore, the values of K_{IC} should be calculated by using the Shetty equation[12].

$$K_{IC} = 0.0889(H \cdot P/4L)^{0.5} \cdot 0.067 H^{0.4} \cdot a^2 \cdot c^{-1.5} \quad (2)$$

where L is the length of crack and a is lattice

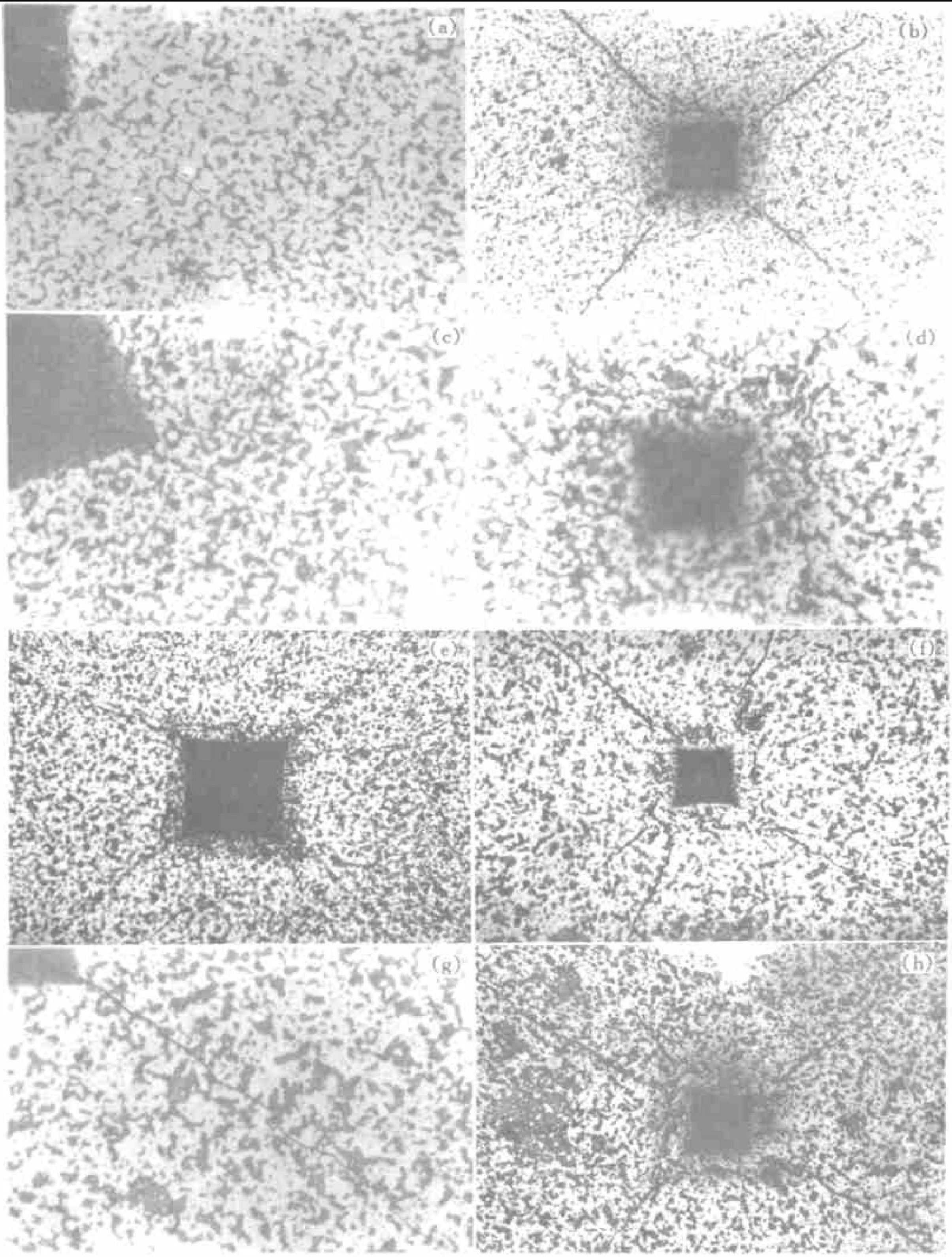

Fig. 4 Cracks morphologies produced by indentation on $MoSi_2$ matrix composites before and after polishing

(a) —$MoSi_2$+ SiC+ $ZrO_2(Y_2O_3)$, before polishing; (b) —$MoSi_2$+ SiC+ $ZrO_2(Y_2O_3)$, after polishing;
(c) —$MoSi_2$+ SiC+ ZrO_2, before polishing; (d) —$MoSi_2$+ SiC+ ZrO_2, after polishing;
(e) —$MoSi_2$+ $ZrO_2(Y_2O_3)$, before polishing; (f) —$MoSi_2$+ $ZrO_2(Y_2O_3)$, after polishing;
(g) —$MoSi_2$+ ZrO_2, before polishing; (f) —$MoSi_2$+ ZrO_2, after polishing

parameter.

The average values of K_{IC} of monolithic $MoSi_2$ and the composites are listed in Table 1. For comparison, the values calculated by using Anstis equation are also illustrated in the same Table. It is clear that all composites have better fracture toughnesses than monolithic $MoSi_2$ does. The composites which exhibit the highest fracture toughness is $MoSi_2$-10% ZrO_2-

Table 1 Mechanical properties of $MoSi_2$ matrix composites

Composites	σ_{bb} /MPa	Hv /GPa	K_{IC}(Anstis) /(MPa·m$^{1/2}$)	K_{IC}(Shetty) /(MPa·m$^{1/2}$)
$MoSi_2$	255	9.0	2.48	2.60
$MoSi_2$-ZrO_2	355	8.1	4.50	4.62
$MoSi_2$-ZrO_2(Y)	258	9.7	2.55	3.76
$MoSi_2$-SiC-ZrO_2	280	9.1	10.19	7.58
$MoSi_2$-SiC-ZrO_2(Y)	525	10.2	4.64	5.05

10% SiC. The K_{IC} value of this composite can reach 7.58 MPa·m$^{1/2}$ based on Shetty equation, and 10.19 MPa·m$^{1/2}$ based on Antis equation. This value is nearly three times that of monolithic $MoSi_2$. It is clear that the composites containing SiC have a higher fracture toughness than that of the composites without SiC. It also appears that when the ZrO_2 powder contains 2.5% Y_2O_3 (mole fraction), the composites have lower fracture toughness.

3.3 Fracture surface analysis

Fig. 5(a) shows a SEM micrograph of the fracture surface of monolithic $MoSi_2$. The surface appears in white and bright, and suggests transgranular fracture. The grain size is fairly large, being approximately 30 μm on average. When compared with the grain size of a few nanometer in $MoSi_2$ monolithic powder, this large grain size clearly shows that $MoSi_2$ undergoes recrystallization and grain coarsening during hot pressing at 1 700 ℃. A large number of pores with diameter smaller than 1 μm were clearly observed on the fracture surface. Since these pores and big grains decrease the cleavage surface energy, they make it easy for transcrystalline crack of the monolithic $MoSi_2$ to happen.

Fig. 5(b) shows a SEM micrograph of the fracture surface of $MoSi_2$ + ZrO_2 composite. It can be seen that small and round ZrO_2 particles are distributed along the grain boundaries of $MoSi_2$, which resists the growth of $MoSi_2$ grains. The grain size of $MoSi_2$ is in the range of 6~ 8 μm. The fracture of this composite occurs mainly through intergranular fracture, but

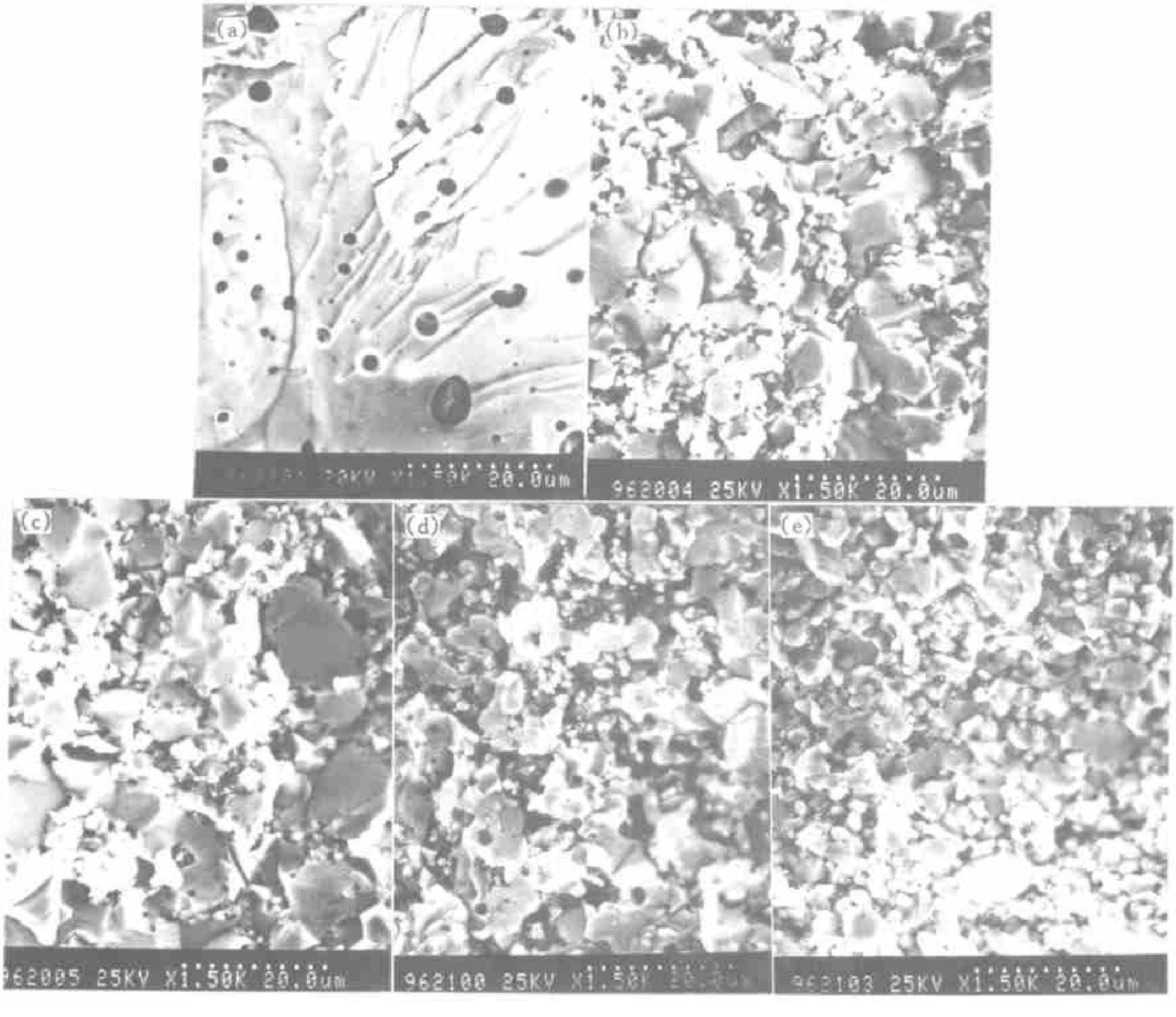

Fig. 5 Fracture morphologies of $MoSi_2$ and its composites
(a) —$MoSi_2$; (b) —$MoSi_2$+ ZrO_2; (c) —$MoSi_2$+ ZrO_2(Y_2O_3); (d) —$MoSi_2$+ SiC+ ZrO_2; (e) —$MoSi_2$+ SiC+ ZrO_2(Y_2O_3)

a small degree of transgranular fracture is also observed. With a very small grain size and intergranular fracture, the crack pathes are significantly prolonged, so more energy is consumed in the process of crack growth, leading to higher fracture toughness.

Fig. 5(c) shows a SEM micrograph of the fracture surface of $MoSi_2$+ ZrO_2(Y_2O_3) composite. Similar to $MoSi_2$+ ZrO_2 composite, the fracture of this composite occurs through both intergranular cracking and transgranular cracking. It appears that the presence of Y_2O_3 prevents ZrO_2 particles from well-distributing along the grain boundaries of $MoSi_2$, so the ZrO_2 particles are less effective in resisting the grain growth, leading to slightly larger $MoSi_2$ grains (the size is approximately 10 μm on average).

Fig. 5(d) and (e) show SEM micrographs of the fracture surface of $MoSi_2$+ SiC+ ZrO_2 and $MoSi_2$+ SiC+ ZrO_2(Y_2O_3) composites respectively. It can be seen that the addition of SiC can further disperse the ZrO_2 particles. The grain size is extremely small, being less than 5 μm. The fracture occurs mainly through intergrannular cracking. It is envisaged that during fracture, the cracks need to bypass both the ZrO_2 particles and SiC particles. With intergrannular fracturing, samll grain size of $MoSi_2$ and small size of ZrO_2 and SiC particles, it is not surprising to see that the $MoSi_2$+ SiC+ ZrO_2 composite has the highest fracture toughness. Once again it appears that the presence of Y_2O_3 in ZrO_2 make the particle more difficult to well disperse in $MoSi_2$, leading to a lower fracture toughness in comparison with the $MoSi_2$+ SiC+ ZrO_2 composite.

4 CONCLUSIONS

1) Four $MoSi_2$ matrix composites, $MoSi_2$ + ZrO_2, $MoSi_2$+ ZrO_2(Y_2O_3), $MoSi_2$+ SiC+ ZrO_2 and $MoSi_2$+ SiC + ZrO_2 (Y_2O_3) are fabricated by the method of mechanical alloying.

2) The cracks produced by indentation on the composites are found to be Palmquist cracks.

3) $MoSi_2$+ SiC+ ZrO_2 composite has the highest fracture toughness, being 7.58 $MPa\cdot m^{1/2}$, and nearly three times that of monolithic $MoSi_2$. This can be attributed to well-distributed ZrO_2 and SiC particles along the boundaries of very fine $MoSi_2$ grains.

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