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In situ synthesis of $Mo(Si,Al)_2$-SiC composites

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An *in situ* reaction was proposed and investigated to produce $Mo(Si_{1-x}Al_x)_2$-SiC composites. The starting powders were $MoSi_2$, Al and C. A direct current hot pressing (DCHP) method was used to prepare these composites. When the mixed powder was hot pressed at temperatures lower than 1500°C, the phase composition was $Mo(Si,Al)_2$ and β-SiC. When the hot pressing temperature was higher than 1600°C, however, Nowotny phase $Mo_{\leq 5}Si_3C_{\leq 1}$ appeared. The chemical stoichiometry of the proposed *in situ* reaction becomes difficult because of the formation of solid solution among these phases and the appearance of Mo_5Si_3C phase. The *in situ* formed SiC phase in the $x = 0.3$ sample was partly in whisker shape. However, the SiC phase in $x = 0.15$ sample was in particle shape. These *in situ* formed SiC particles and whiskers acted as crack deflection and bridging elements and improved the fracture toughness. The Vickers hardness and fracture toughness of the $x = 0.3$ sample hot pressed at 1700°C for 60 min in vacuum were 15.6 GPa and 5.39 $MPa \cdot m^{1/2}$, respectively.

1. Introduction

Molybdenum disilicide ($MoSi_2$) is generally used as a heating element up to 1700°C in an air atmosphere. Recently, it has been recognized as a potentially useful matrix material for high temperature structural ceramic composites. Monolithic $MoSi_2$ material is brittle at room temperature and has low creep resistance at high temperatures. However these disadvantages can be reduced by compositing. For example, the research work about the addition of second phases such as SiC or Al_2O_3 fibers [1, 2], SiC whiskers [3], SiC particles [4, 5], ZrO_2 [6], Al_2O_3 [7, 8], Mo_2B_5 [9], TiB_2, TiN, B_4C [10] and Mo_2C [11] *et al*. have been reported. The methods used for the addition of these second phases can be generally divided into two groups: direct addition or *in situ* formation by chemical reaction. Henager *et al*. proposed to use the reaction $Mo_2C + 5Si \rightarrow 2MoSi_2 + SiC$ to produce an $MoSi_2$-SiC composite [5, 12], Krishnarao *et al*. used the reaction between SiO_2 or Si_3N_4 and Mo and C to produce $MoSi_2$-SiC composites [13], Costa e Silva *et al*. used the reaction $Mo_5Si_3 + B \rightarrow MoSi_2 + Mo_2B_5$ (or MoB) to produce $MoSi_2$-molybdenum boride composites [14] and Tilly *et al*. synthesized $MoSi_2$-SiC composites by melt processing from high purity Mo, Si and C element sources [15, 16]. Most recently, Hecht *et al*. prepared a $MoSi_2$/SiC nanocomposite by *in situ* pyrolysis of $MoSi_2$ particles coated with polycarbosilane and subsequent densification by hot pressing [17]. In addition, Watanabe *et al*. [18] found that $MoSi_2/Mo_2B_5$ composites showed superplasticity at about 1400°C and Zhang *et al*. [19, 20] utilized this behavior to design high temperature multilayer composites with superplastic interlayers.

On the other hand, it has been reported that the aluminum addition and the $Mo(Si,Al)_2$ formation could improve the mechanical properties and oxidation resistance of $MoSi_2$ [21–24]. The pesting (a type of destructive oxidation) of $MoSi_2$ at about 500°C can be suppressed by the addition of Al because the volume change in the process of oxidation is largely reduced [22]. The high temperature oxidation properties of $MoSi_2$ can also be improved by the addition of Al and formation of $Mo(Si,Al)_2$. The formation of Al_2O_3 in the oxidation process can restrict the crystallization of SiO_2, which also forms in the oxidation process [21]. Shobu *et al*. [25] studied the SiC-$Mo(Si,Al)_2$ composites prepared by melt infiltration of $Mo(Si,Al)_2$ into porous SiC preform. The composites exhibited moderate strength (up to about 600 MPa) up to 1600°C for fast fracture. In this paper, the preparation and the mechanical properties at room temperature of a $Mo(Si,Al)_2$-SiC composite by *in situ* process is reported. The proposed *in situ* reaction is:

$$MoSi_2 + 2xAl + 2xC \rightarrow Mo(Si_{1-x}Al_x)_2 + 2xSiC \quad (1)$$

2. Experimental procedure

The starting powders were $MoSi_2$ (mean particle size 6 μm, main impurities were oxygen 0.21, Fe 0.17 and

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C 0.03 wt%), aluminum (purity 99.9%) and C (purity 99.9%). In the present study, the value of x in reaction (1) was set to be 0.15 and 0.3. The raw powders with stoichiometric compositions according to reaction (1) were mechanically dry mixed using an Al_2O_3 mortar for 1 h. The mixed powders were then hot pressed using a direct current hot press (DCHP) machine [26] at 1300°C, 1400°C, 1500°C, 1600°C and 1700°C under 20 MPa in a vacuum for 60 min. For comparison, monolithic $MoSi_2$ was also prepared by DCHP at 1600°C under 20 MPa in a vacuum for 60 min using the same raw powder of $MoSi_2$. The surface layer of the hot pressed specimens were ground away and their densities were measured by the water displacement method. The phase compositions of the specimens were determined by X-ray diffraction (XRD) using CuK_α radiation. The Vickers hardness (Hv) and fracture toughness (K_{IC}) was tested by indentation technique using an indent load of 196 N on the polished surfaces of the specimens. The Evans and Charles formula [27] was adopted to calculate the fracture toughness. Each data was an average of 6 values. Scanning electron microscopy (SEM) was used to observe the microstructures of the materials. Energy-dispersive X-ray analysis (EDAX) associated with SEM was used to determine phase chemistry.

3. Results and discussion

3.1. Phase compositions

The XRD patterns of the hot pressed specimens are shown in Fig. 1. From Fig. 1 it can be seen that when the hot pressing temperatures were lower than 1500°C, the phase composition was $Mo(Si,Al)_2$ and β-SiC. However, at 1600°C the Nowotny phase $Mo_{\leqq 5}Si_3C_{\leqq 1}$ (which is written as Mo_5Si_3C) appeared and the product became a ternary-phase composite. At 1700°C the intensity of XRD peaks of Mo_5Si_3C phase became stronger and it showed that more Nowotny phase had formed or possibly the crystallization of this phase improved with increasing hot pressing temperatures. This Nowotny phase generally appears when carbon exists in the composition [13, 28] and it is considered that this phase can be used as a reinforcement [29]. In this situation, however, the chemical reaction was more complex than reaction (1). According to the EDAX results by SEM, Mo, Si and Al elements existed in all of these three phases. Fig. 2 shows the EDAX pattern of SiC phase (the black region in SEM photos which will be discussed later) in the specimen with $x = 0.3$ hot pressed at 1700°C. This means that the chemical stoichiometry in reaction (1) becomes difficult because of the formation of solid solution. According to the results obtained in $MoSi_2$-Al reaction system [24], Al would begin to displace Si and form $Mo(Si,Al)_2$ at as low temperature as 680°C, the following reaction sequence can be suggested:

$$MoSi_2 + Al \rightarrow Mo(Si_{1-x}Al_x)_2 + Si \quad (2)$$

$$Si + C \rightarrow SiC \quad (3)$$

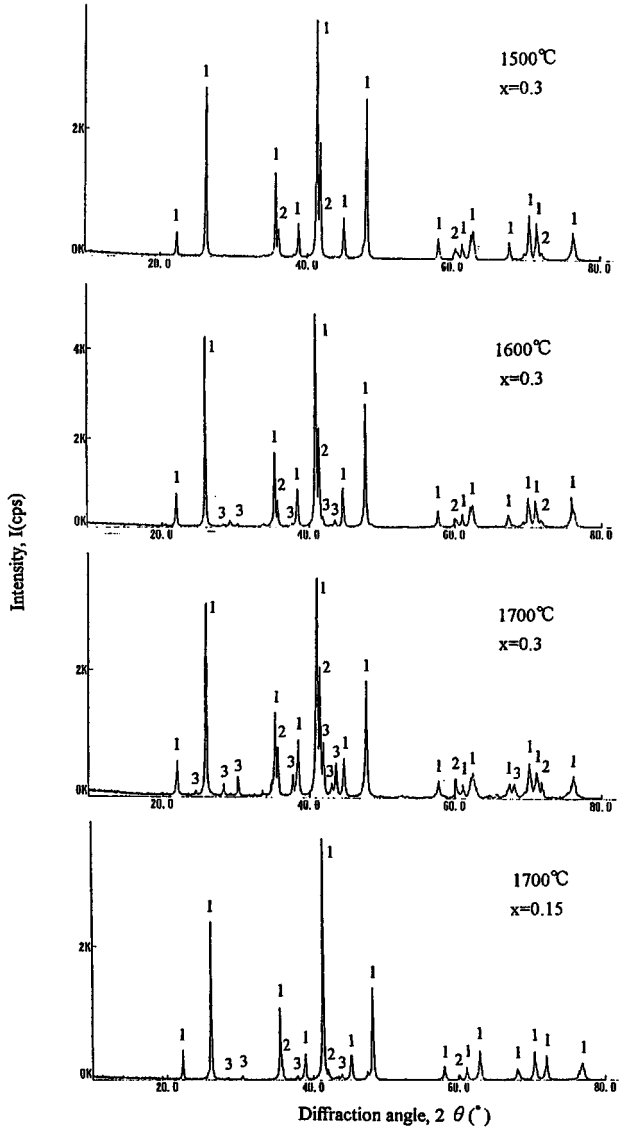


Figure 1 XRD patterns of the specimens hot pressed at various temperatures for 60 min under 20 MPa in a vacuum (1—$Mo(Si,Al)_2$; 2—SiC; 3—Mo_5Si_3C).

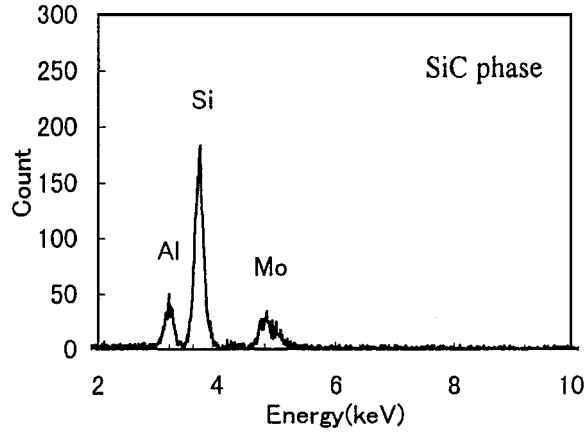


Figure 2 The EDAX pattern of SiC phase in $x = 0.3$ specimen hot pressed at 1700°C for 60 min.

At high temperatures above 1500°C,

$$Mo(Si_{1-x}Al_x)_2 + SiC \rightarrow Mo(Si_{1-y}Al_y)_2 + Mo_5Si_3C \quad (4)$$

Further work investigating the details of the reaction mechanism and the relationship between the element

composition and the properties of the materials obtained in this system needs to be done. However, it is suggested that the reaction mechanism is different with that in the Mo_2C-Si displacement reaction system [5]. Also, because the state and distribution of the *in situ* formed Si from reaction (2) should be different with that of directly added one, it is believed that SiC formed through *in situ* reactions (2) and (3) is easy to grow as whisker-like (microstructures are shown in next section).

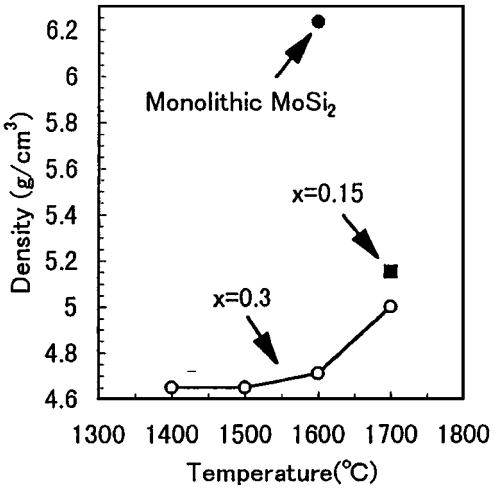


Figure 3 Relationship between the densities of the specimen and hot pressing temperatures.

From Fig. 1 one can also see that the XRD peak (111) of $Mo(Si,Al)_2$ with $x = 0.15$ and $x = 0.3$ are different. In $x = 0.3$ sample, there was a diffraction peak with a little large diffraction angle near the (111) peak. This peak did not exist in the $x = 0.15$ specimen. Although the diffraction peak (200) of β-SiC is at this angle, the intensity should not be as high. It was preliminarily suggested that this peak was related to the $Mo(Si,Al)_2$ phase with high x values.

3.2. Microstructures

Fig. 3 shows the relationship between the densities of the specimens and hot pressing temperatures. The density of monolithic $MoSi_2$ hot pressed at 1600°C was 6.23 g/cm^3 (98.73% of theoretical density). It can be seen that the rapid increase of densification occurred in the temperature range of 1600°C to 1700°C. Although it is difficult to know the theoretical density of the material and hot pressing temperature higher than 1700°C was limited by the hot pressing machine. The

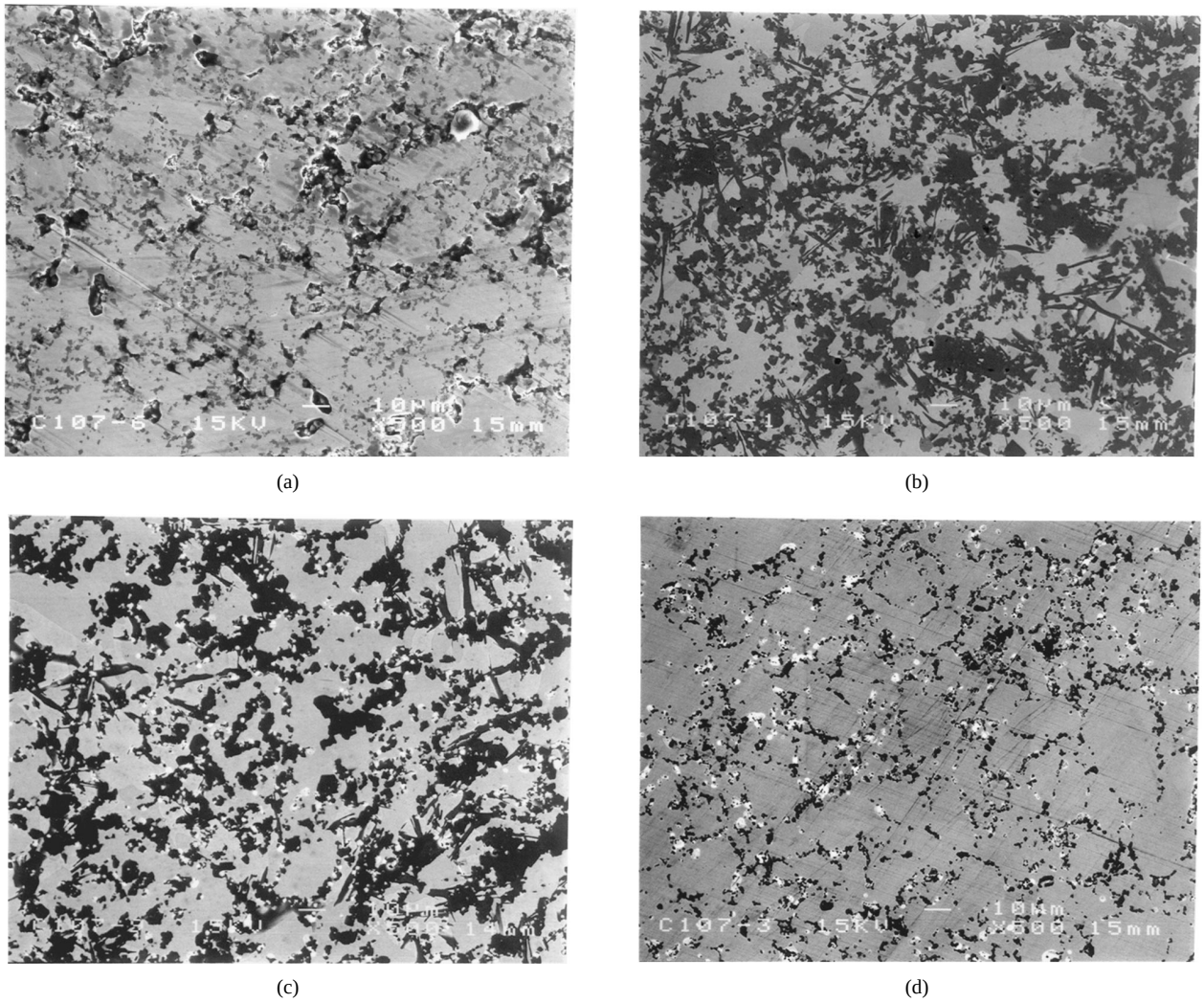
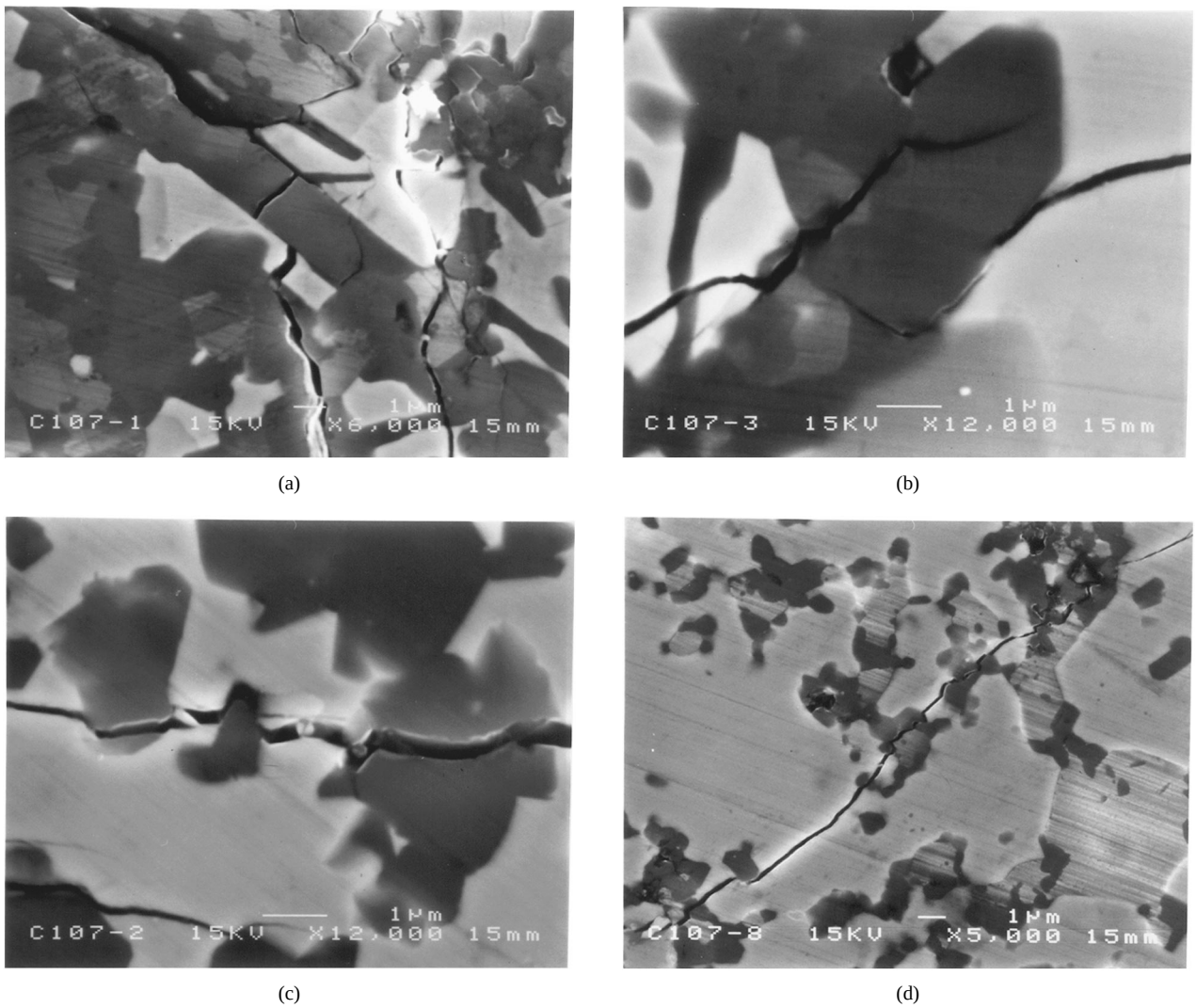


Figure 4 SEM photographs of the polished surfaces of the specimens. Black phase is SiC. (a) hot pressed at 1600°C and vertical to the hot pressing direction, $x = 0.3$; (b) hot pressed at 1700°C and vertical to the hot pressing direction, $x = 0.3$; (c) hot pressed at 1700°C and parallel to the hot pressing direction, $x = 0.3$; (d) hot pressed at 1700°C and vertical to the hot pressing direction, $x = 0.15$.

densification of the specimens which were hot pressed at 1700°C for 60 min were satisfied according to the SEM observation. Fig. 4 shows the SEM photographs of the polished surfaces of the specimens. It can be seen that when the hot pressing temperature was at 1600°C, some large pores remained in the specimen and the *in situ* formed SiC was in particle shape (Fig. 4a). For the specimen with $x = 0.3$ and hot pressed at 1700°C, almost no pores remained in the specimen and many of the *in situ* formed SiC particles were in whisker shape. Fig. 4b and c are the SEM micrographs of the surfaces, vertical and parallel to hot pressing direction respectively for the specimen with $x = 0.3$ and hot pressed at 1700°C. In the vertical direction the SiC particles appeared larger and more whisker like than that in the parallel direction, and it is suggested that the *in situ* formed SiC is whisker shaped. The SEM photo of the specimen with $x = 0.15$ which was hot pressed at 1700°C is shown in Fig. 4d and it can be seen that the *in situ* formed SiC particles had particulate shape and were very fine in size (less than 2 μm). It also seemed that the *in situ* formed SiC particles were located at the grain boundaries of the $Mo(Si,Al)_2$ matrix and formed a three-dimension SiC chain. The distribution pattern of the *in situ* formed SiC particles should inhibit the grain growth of the $Mo(Si,Al)_2$ matrix. On the other hand, the

TABLE I Mechanical properties of the *in situ* composites

Sample		DCHP at 1600°C, $x = 0.3$	DCHP at 1700°C, $x = 0.3$	DCHP at 1700°C, $x = 0.15$	Monolithic $MoSi_2$
Vickers	⊥DCHP	4.4	15.6	11.6	6.0
hardness (GPa)	//DCHP	—	10.5	9.2	—
Fracture toughness	⊥DCHP	3.2	5.39	2.61	1.82
($MPa \cdot m^{1/2}$)	//DCHP	—	3.44	2.43	—



(a) (b) (c) (d)

Figure 5 The interactions of *in situ* formed SiC particles and whiskers with the Vickers indent induced propagating cracks. (a), (b) and (c) shows the crack deflection and bridging by the *in situ* formed SiC particles and whiskers in $x = 0.3$ specimen hot pressed at 1700°C; (d) shows the crack deflection in $x = 0.15$ sample hot pressed at 1700°C.

in situ formed Mo_5Si_3C was lighter in color when compared with $Mo(Si,Al)_2$ in the SEM photographs and it was not easy to distinguish.

3.3. Mechanical properties and toughening mechanism

The mechanical properties of the hot pressed specimens are shown in Table I. The Vickers hardness measured for the monolithic $MoSi_2$ was lower than reported [2], which may have been caused by the slightly higher porosity observed in the specimen. The Vickers hardness and fracture toughness (in the direction vertical to the hot pressing) of the specimen with $x = 0.3$ and hot pressed at 1700°C were much higher than that for the monolithic $MoSi_2$ material. These properties were obviously lower in the direction parallel to the hot pressing because the *in situ* formed SiC whiskers grew mainly in the vertical direction. This property difference in different direction was not so obvious for the specimen with $x = 0.15$ because the *in situ* formed SiC in this specimen had particulate shape. Fig. 5 shows the interactions of *in situ* formed SiC particles and whiskers with the Vickers indent induced cracks. It can be seen that the *in situ* formed SiC could act as bridging and deflection elements in both the particle shape or whisker shape. The *in situ* formed fine SiC particles in the specimen with $x = 0.15$ could also act as a deflection element as shown in Fig. 5d. Thus, the toughening mechanism in these *in situ* $Mo(Si,Al)_2$-SiC composites was suggested to be crack deflection and bridging by *in situ* formed SiC particles and whiskers. Henager *et al.* [5] found that the highest toughness was measured for materials hot pressed at shorter times and having smaller SiC volume fraction in $MoSi_2$-SiC system from Mo_2C-Si reaction. In the present case, however, because the shapes of the *in situ* formed SiC in $x = 0.3$ specimen (whisker shaped) and $x = 0.15$ specimen (particle shaped) were different, the effect of SiC content on fracture toughness should be different with that observed in the $MoSi_2$-SiC composites from Mo_2C-Si reaction system.

4. Conclusions

$Mo(Si,Al)_2$-SiC composites were prepared by *in situ* reaction of $MoSi_2$, Al and C. The phase composition of the specimens hot pressed at temperatures lower than 1500°C consisted of $Mo(Si,Al)_2$ and β-SiC. When the hot pressing temperature was higher than 1600°C, Mo_5Si_3C appeared. Because of the solid solution between these phases and the formation of Mo_5Si_3C the chemical stoichiometry of the proposed *in situ* reaction becomes impossible. When hot pressed at 1700°C the *in situ* formed SiC for $x = 0.3$ specimen had partly in whisker morphology, and for the $x = 0.15$ specimen the SiC had particulate shape. These SiC particles and whiskers could act as deflection and bridging elements and improved the toughness of the composites. The Vickers hardness and fracture toughness (in the vertical direction to hot pressing) of the $x = 0.3$ specimen hot pressed at 1700°C for 60 min were 15.6 GPa and 5.39 $MPa \cdot m^{1/2}$, respectively. The mechanical properties in the direction parallel to the hot pressing were lower than those in the vertical direction.

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