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Experiments on packing and sintering of composite powder mixtures of $MoSi_2 + Al_2O_3$ platelets

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Abstract

The packing and pressurelessly sintering behaviors of $MoSi_2 + Al_2O_3$ platelets composite powder mixtures were studied in this paper. The experimental results show that a higher green density of this mixture can be obtained by mixing $MoSi_2$ powders with different particle sizes and the green density can be more improved by adding finer $MoSi_2$ powders to the $MoSi_2$ matrix. The pressurelessly sintering behaviors are very different for the samples on the different layers even in a small closed crucible. A large weight loss occurred during sintering, which evidently reduced the relative density of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite. A 88.6% of relative density of this composite can be obtained by pressurelessly sintering the billets with the highest green relative density of 60.3% in argon at 1700°C×2 h. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved.

Keywords: B. Platelets; D. Al_2O_3; Packing; Pressureless sintering; $MoSi_2$

1. Introduction

The intermetallic compound molybdenum disilicide ($MoSi_2$) has a number of properties which make it attractive as a matrix material in structural composites. Several attempts have been made to increase both the low temperature toughness and the elevated temperature creep resistance of $MoSi_2$ [1–3]. Owing to the cost of whiskers and the health problems for whisker reinforcing and the effectiveness being dependent on the transformation temperature for ZrO_2 phase transformation toughening, increasing attention has recently been devoted to platelet addition [4,5].

It is well-recognized that the green microstructure of a powder compact has a tremendous effect on the sintering behavior. Powder compact densification can be enhanced by using samples with more homogeneous particle packing and higher green relative density. A high maximum packing density is directly dependent upon the particle size distribution. Many studies have demonstrated the importance of the particle size distribution on obtaining dense packing [6–8]. Generally, the green compacts with higher relative density can be obtained by using the broad size distribution powders.

Considering the void volume associated with a unit volume of packed bed formed when the particles of largest size are permitted to pack, if particles of sufficiently small size are now added, it is evident that these could be placed in the original voids associated with the large particles. The net effect will be an increase in the number of particles present without any overall increase in volume of the packed bed. In principle this process can be repeated by adding a third, fourth, etc., component of sufficiently small size that the particles will fit into the void space associated with the next larger particle. Thus, the blending of particles of appropriate size will, in general, lead to an increase in the packing density of the bed. Furthermore, it is also evident that at some ratio of large to small particle size as well as at some fraction of the large to small component, the packing density will reach a maximum. For large particles, the void fraction for a single component is about 0.37 for a randomly packed bed. This void fraction is equivalent to that for an ordered packed bed containing equal fraction of cubic packing or of hexagonal closed-packing. If this mixture of ordered packing can be taken as a model for the randomly packed bed, then it is easy to show that the maximum size ratio of spheres that can be

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accommodated in the interstitial void of that fraction of the bed in cubic packing is about 0.41, while the size ratio for the corresponding hexagonal close pack is 0.15. The average value of the size ratio is thus about 0.3. On the basis of this estimate, which is probably too high, the size of small particles should be about four times smaller than that of large particles [7].

The objects of this paper are to try to improve the green density of $MoSi_2 + Al_2O_3$ platelets composite mixtures by using different size $MoSi_2$ powders and pressurelessly sinter this kind of composite.

2. Experimental

The raw materials selected for investigation were $MoSi_2$ powders with an as received mean particle diameter of 2.5 μm, Al_2O_3 platelets with an average diameter of 10–15 μm and 0.6 μm in thickness. The principal impurities of $MoSi_2$ powders and Al_2O_3 platelets are shown in Table 1. The as-received $MoSi_2$ powders were attrition milled for 24 h, 48 h and 72 h, respectively. The stirring speed was 500 rpm, the radio of ball (Al_2O_3 balls with a diameter of 1.5–2mm) charge vehicle (distilled water) was 5:1:4 by volume with 0.1 wt% Darvan C as a disperser. The $MoSi_2$ powders solvent was dried and sieved with 100 mesh after milling. A JEOL JSM-84A type of SEM and a Horiba Capa-700 type of Particle Size Distribution Analyzer were used to determine the particle size distribution of as received and after milling powders. The powders were dispersed in water with 0.4 wt% Darvan C by stirring more than 30 min, which made sure that the powders were dispersed well in the solvents before determining.

The as received $MoSi_2$, refined $MoSi_2$ powders and Al_2O_3 platelets were mixed with the same Al_2O_3 platelets content (25 vol%) but different refined $MoSi_2$ powders contents, then inserted into a plastic bottle together with Al_2O_3 balls (Al_2O_3 balls with a diameter of 3 mm), distilled water and 0.5 wt% Darvan C, the ratio of ball charge vehicle was 1:1:1 by weight. The mixtures were then ground for 24 h at low speed and after rotovap drying at 130°C and 90 rpm and sieving by 100 mesh were uniaxially pressed at 250 MPa. The uniaxially pressed billets were cold isostatically pressed at 400 MPa for 10 s. The green density of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite mixtures was calculated by measuring its weight and volume. Al_2O_3 powders (3.5 wt%) were introduced into $MoSi_2$ powders after milling for 72 h, which had been considered in mixing $MoSi_2 + 25$ vol% Al_2O_3 platelets composite mixtures.

Table 1
Principal impurities of $MoSi_2$ powders and Al_2O_3 platelets (in wt%)

$MoSi_2$		Al_2O_3	
O	1–2	F	3.2
Al	1300 ppm	Si	0.55
Fe	900 ppm	Li	0.5
Mn	600 ppm	Fe	350 ppm

One of the billets with the highest green density was sintered pressurelessly in argon at 1650, 1700 and 1750°C for 2 h, respectively. The heating speed was 12°C/min, cooling speed 17°C/min. The billets were put into a closed alumina crucible and covered by Al_2O_3 powders during sintering. The densities of the specimens were determined by the Archimedes method after absorbing xylene. The density and porosity were calculated in the following equations:

$$\rho = \text{density} = \frac{Wa}{\frac{Wa - Wxw}{\rho_w}} \tag{1}$$

$$\text{O.P.} = \text{open porosity} = \frac{\frac{Wxa - Wa}{\rho_x}}{\frac{Wxa - Wxw}{\rho_w}} \times 100\% \tag{2}$$

$$\text{T.P.} = \text{total porosity} = \frac{(Wxa - Wxw) - \left(\frac{Wa}{\rho_{\text{th}}} \times \rho_w\right)}{Wxa - Wxw} \times 100\% \tag{3}$$

Wa = sample weight in air, Wxa = sample with xylene weight in air, Wxw = sample with xylene weight in water, ρ_w = density of distilled water, ρ_x = density of xylene = 0.88 g/cm^3, ρ_{th} = theoretical density of the sample = 5.69 g/cm^3 for $MoSi_2 + 25$ vol% Al_2O_3 platelets composite.

3. Results and discussion

3.1. Refining $MoSi_2$ particles

The particle size distributions of the as received and attrition milled $MoSi_2$ powders are shown in Figs. 1 and 2 and Table 2. The mean diameters of $MoSi_2$ powders summarized in Table 2 were measured by SEM technique. It can be found that the mean diameter of as-received $MoSi_2$ powders (2.57 μm) is very close to the data (2.5 μm) from the vendor. The particle sizes become finer and finer with increment of the attrition milling time. The mean diameter of $MoSi_2$ powders after milling 72 h is 0.56 μm and there are more finer $MoSi_2$ particles in the particle size distribution as shown in Figs. 1(d) and 2(b2). The median diameter of $MoSi_2$ powders after milling 72 h determined by particle size distribution analyzer (0.2 μm) was very different from that measured by SEM (0.56 μm).

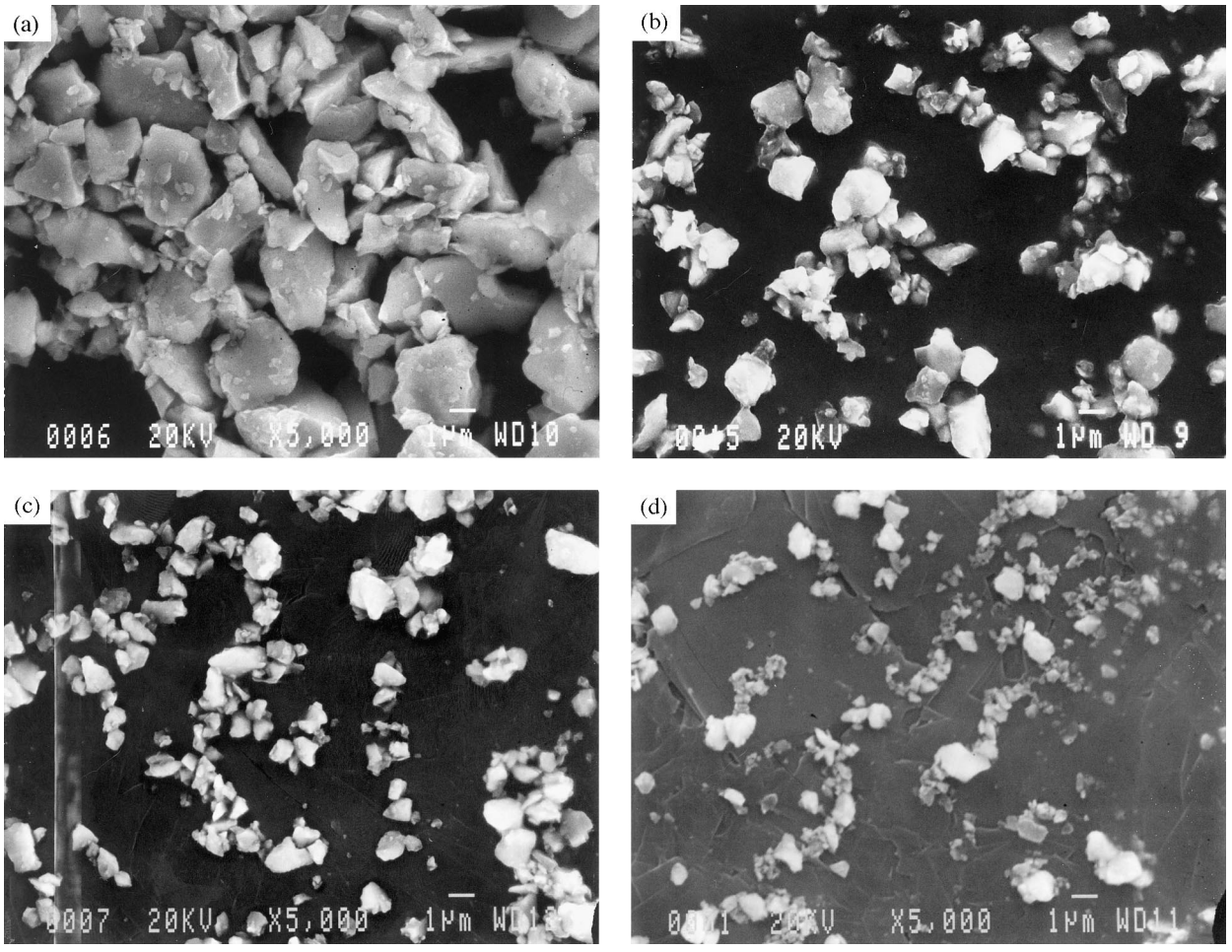

Fig. 1. SEM photographs of the particle size distributions of $MoSi_2$ powders as-received and after attrition milling. (a) as-received; (b) milling 24 h; (c) milling 48 h; (d) milling 72 h.

Table 2
The mean diameters of as received and attrition milled $MoSi_2$ powders

Attrition milling time (h)	0	24	48	72
Mean diameter of $MoSi_2$ (μm)	2.57	1.38	0.83	0.56

3.2. Packing of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite powder mixtures

The green densities of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite (defined as MA25) powder mixtures with 10 vol% $MoSi_2$ powders which were attrition milled for different time are shown in Table 3. The theoretical density of MA25 is 5.69 g/cm^3 which was obtained according to the mixture law. The results show that the green density of MA25 can be obviously increased by adding 10 vol% refined $MoSi_2$ powders. The increment of the green density is bigger when the particle size of the refined $MoSi_2$ powders is smaller. But the addition of 10 vol% $MoSi_2$ powders after milling 72 h leads to a much lower increment of the green density of MA25. This is because the $MoSi_2$ particles are not easy to be refined further after milling 48 h, and as much as 3.5 wt% Al_2O_3 powders from the Al_2O_3 balls was introduced into the refined $MoSi_2$ powders during the milling so that the milling time was not longer than 72 h in this paper.

It could be found that the green density of MA25 can be improved by increasing the uniaxially pressing load. It can be increased from 2.59 g/cm^3 at P = 100MPa to 2.72 g/cm^3 at P = 250 MPa for MA25 with 10 vol% milling 48 h $MoSi_2$ powders. But the green densities become almost the same after cold isostatically pressing at the same load of 400 MPa, 3.31 g/cm^3 and 3.32 g/cm^3, respectively. The green density of MA25 with 10 vol% milling 72 h $MoSi_2$ powders can be improved to 3.36 g/cm^3 if the green billets were cold isostatically pressed at P = 400 MPa twice. This means that longer holding load time is beneficial to the improvement of the green density. A load of 250 MPa for uniaxially pressing and 400 MPa for cold isostatically pressing once (about 10 s) were selected in the following work.

The green densities of MA25 with different milling 72 h $MoSi_2$ powders contents after uniaxially pressing

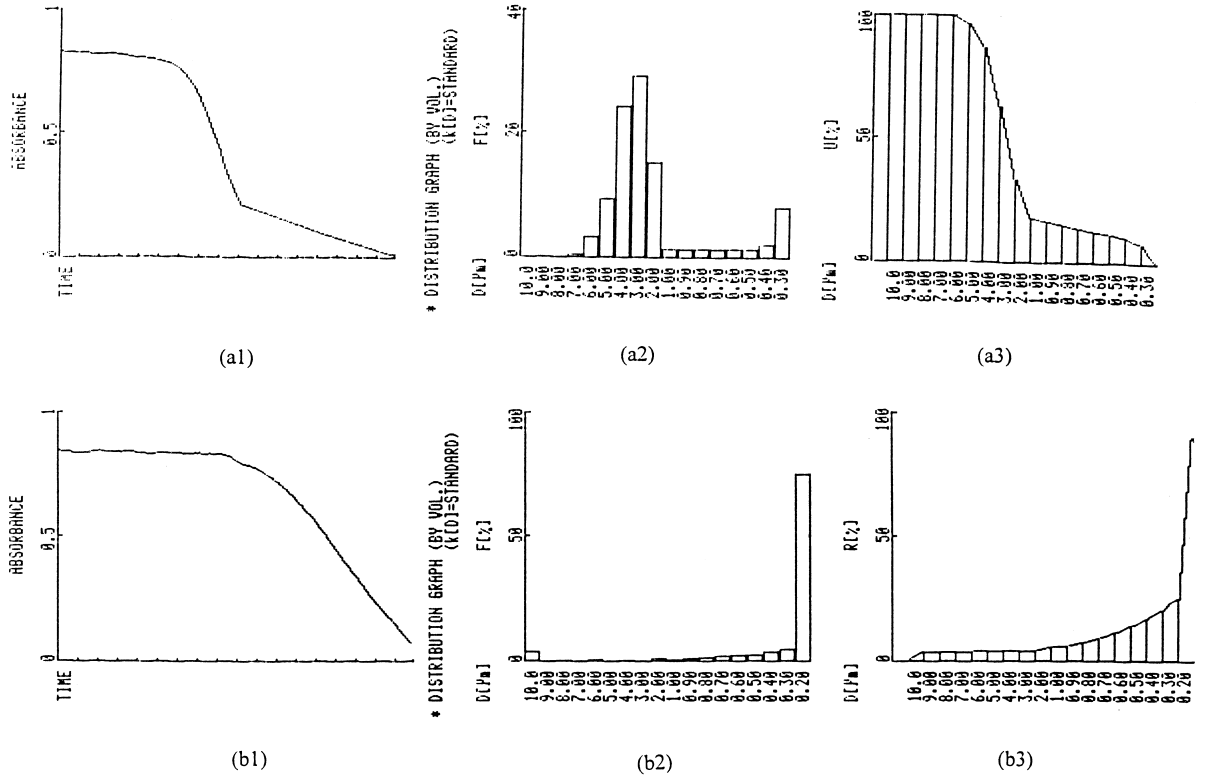

Fig. 2. The particle size distributions of $MoSi_2$ powders as-received and after attrition milling. (a) as-received, $d_{50} = 2.57$ μm; (b) milling 72 h, $d_{50} = 0.20$ μm.

Table 3
The green density of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite powder mixtures

	Uniaxially Press P = 250 MPa	CIP P = 400 MPa
MA25, 100 vol% as received $MoSi_2$	2.68g/cm^3	3.22g/cm^3
	47.1%	56.6%
	(P = 100MPa)	
MA25, (90% as-received + 10% milling 24 h) $MoSi_2$	2.56g/cm^3	3.24g/cm^3
	45.0%	56.9%
MA25, (90% as-received + 10% milling 48 h) $MoSi_2$	2.72g/cm^3	3.32g/cm^3
	47.8%	58.3%
MA25, (90% as-received + 10% milling 72 h) $MoSi_2$	2.73g/cm^3	3.32g/cm^3
	48.0%	58.3%

(90% as-received + 10% milling 24 h) $MoSi_2$—means that 90% $MoSi_2$ is from as-received, 10% $MoSi_2$ is from attrition milled for 24 h.

and cold isostatically pressing are shown in Table 4 and Fig. 3. It can be found that the green relative density (measured density divided by calculated theoretical density) of pure as received $MoSi_2$ powders is 58.3%, but it is decreased to 56.6% by adding 25 vol% Al_2O_3 platelets. It is seen that the addition of Al_2O_3 platelets slightly decreases the green relative density of $MoSi_2$ matrix due to the geometric incompatibility of these two particles. However, the green relative density of MA25 can be obviously improved by adding refined $MoSi_2$ powders, which is continuously increased with the increment of refined $MoSi_2$ powders content at first and reaches a maximum value of 60.3% at 50 vol% milling 72 h $MoSi_2$ powders. The further increment of the refined $MoSi_2$ powders leads, on the other hand, to a decrease in the green relative density, 60.1% for 60 vol% refined $MoSi_2$ powders and 58.9% for 100 vol% refined $MoSi_2$ powders. But it is still much higher than that of as-received $MoSi_2 + 25$ vol% Al_2O_3 platelets mixture. According to the Furnas model [6], the maximum density was obtained when the content of finer powders was 33 vol% in a binary system. The result shown in this paper is very close to it. The maximum green density of MA25 was obtained at 50 vol% refined $MoSi_2$ powders in $MoSi_2$ matrix, but at 37.5 vol% refined $MoSi_2$ powders in total MA25. The green billet of MA25 with maximum relative density was selected to investigate its pressurelessly sintering behaviors in the following work.

Table 4
The green density of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite powder mixtures

	Uniaxially Press P = 250 MPa	CIP P = 400 MPa
Pure $MoSi_2$	2.99g/cm^3	3.65g/cm^3
	47.8%	58.3%
MA25, 100% as-received $MoSi_2$	2.68g/cm^3	3.22g/cm^3
	47.1%	56.6%
MA25, (95% as-received + 5% refined) $MoSi_2$	2.72g/cm^3	3.27g/cm^3
	47.8%	57.5%
MA25, (90% as-received + 10% refined) $MoSi_2$	2.73g/cm^3	3.32g/cm^3
	48.0%	58.3%
MA25, (80% as received + 20% refined) $MoSi_2$	2.79g/cm^3	3.37g/cm^3
	49.1%	59.3%
MA25, (70% as received + 30% refined) $MoSi_2$	2.79g/cm^3	3.38g/cm^3
	49.1%	59.4%
MA25, (60% as received + 40% refined) $MoSi_2$	2.85g/cm^3	3.41g/cm^3
	50.1%	59.9%
MA25, (50% as received + 50% refined) $MoSi_2$	2.84g/cm^3	3.43g/cm^3
	49.9%	60.3%
MA25, (40% as received + 60% refined) $MoSi_2$	2.79g/cm^3	3.42g/cm^3
	49.0%	60.1%
MA25, 100% refined $MoSi_2$	2.53g/cm^3	3.35g/cm^3
	44.5%	58.9%

The refined $MoSi_2$ powders are obtained by attrition milling 72 h.

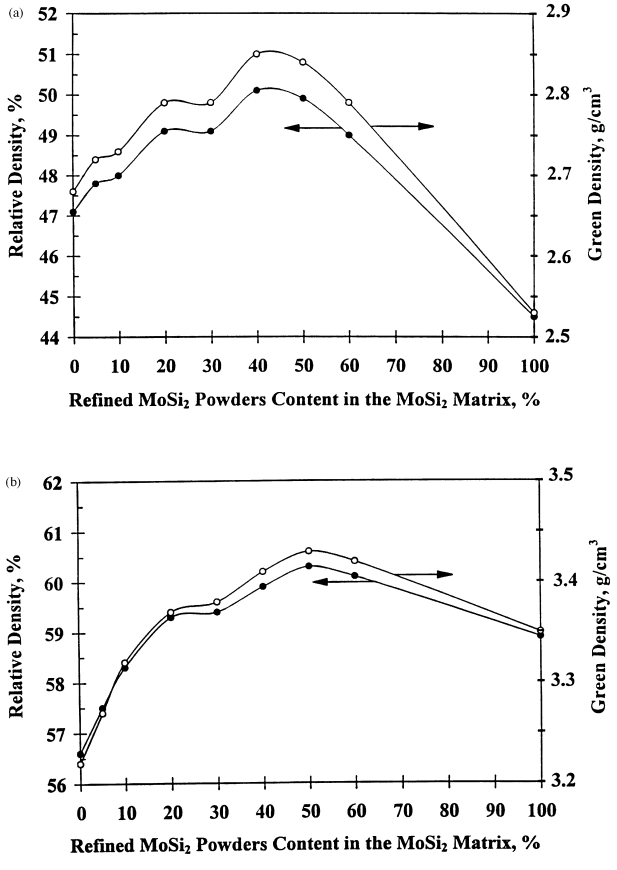

Fig. 3. The green density of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite powders mixtures (a) after uniaxially pressed at P = 250 MPa; (b) after cold isostatically pressed at P = 400 MPa.

3.3. Pressurelessly sintering behaviors of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite

The green billets of MA25 with the relative density of 60.3% were sintered pressurelessly at 1650, 1700 and 1750°C for 2 h in argon, respectively. The densities and some other important parameters after sintering are summarized in Tables 5–7. It can be seen that the sintering behaviors of the samples on different layers in a closed crucible are very different even at the same temperature. The positions of the samples in the closed crucible are schematically shown in Fig. 4. The samples on the first layer always have the lowest densities, weight loss and highest total porosity, but the samples on the third layer always have the highest densities, weight loss and lowest total porosity after sintering except that at 1750°C the samples on the third layer have a lower density than that on the second layer because a larger weight loss can result in the evident decrease in density at such a high temperature. If we compare with the samples at the same layer sintering at different temperatures, it can be found that on every layer the samples reach a maximum relative density when sintering at 1700°C, then the relative density decreases when sintering at a higher temperature (1750°C). A relative density of 88.6% for $MoSi_2$ + 25 vol% Al_2O_3 platelets composite can be obtained by sintering pressurelessly.

The large weight losses shown in Tables 5–7 must have arisen from some active oxidation. Because of lack of oxygen in the sintering atmosphere one possible reaction that could have occurred during densification was as following:

Table 5
Pressurelessly sintering behaviors of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite at 1650°C

	Density	Total porosity	Open porosity	Weight loss
	4.92 g/cm^3			
On third layer	86.5%	13.60%	4.05%	5.6%
	4.88 g/cm^3			
On second layer	85.8%	14.20%	1.20%	2.4%
	4.80 g/cm^3			
On first layer	84.4%	15.60%	0.46%	1.3%

Table 6
Pressurelessly sintering behaviors of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite at 1700°C

	Density	Total porosity	Open porosity	Weight loss
	5.04 g/cm^3			
On third layer	88.6%	11.50%	4.17%	6.8%
	5.00 g/cm^3			
On second layer	87.9%	12.06%	1.22%	3.1%
	4.86 g/cm^3			
On first layer	85.4%	14.64%	0.59%	0.7%

Table 7
Pressurelessly sintering behaviors of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite at 1750°C

	Density	Total porosity	Open porosity	Weight loss
	4.28 g/cm^3			
On third layer	75.2%	24.86%	22.56%	11.1%
	4.71 g/cm^3			
On second layer	82.8%	17.20%	6.53%	3.4%
	4.35 g/cm^3			
On first layer	76.4%	23.63%	11.83%	0%

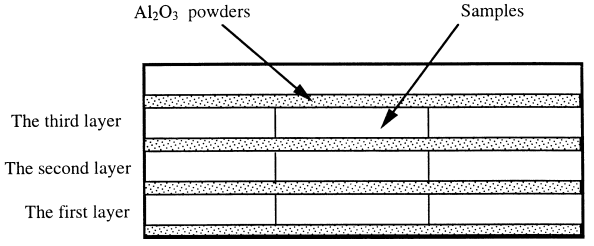

Fig. 4. Schematic presentation of the sample position in a closed alumina crucible of 45×100×38 mm^3.

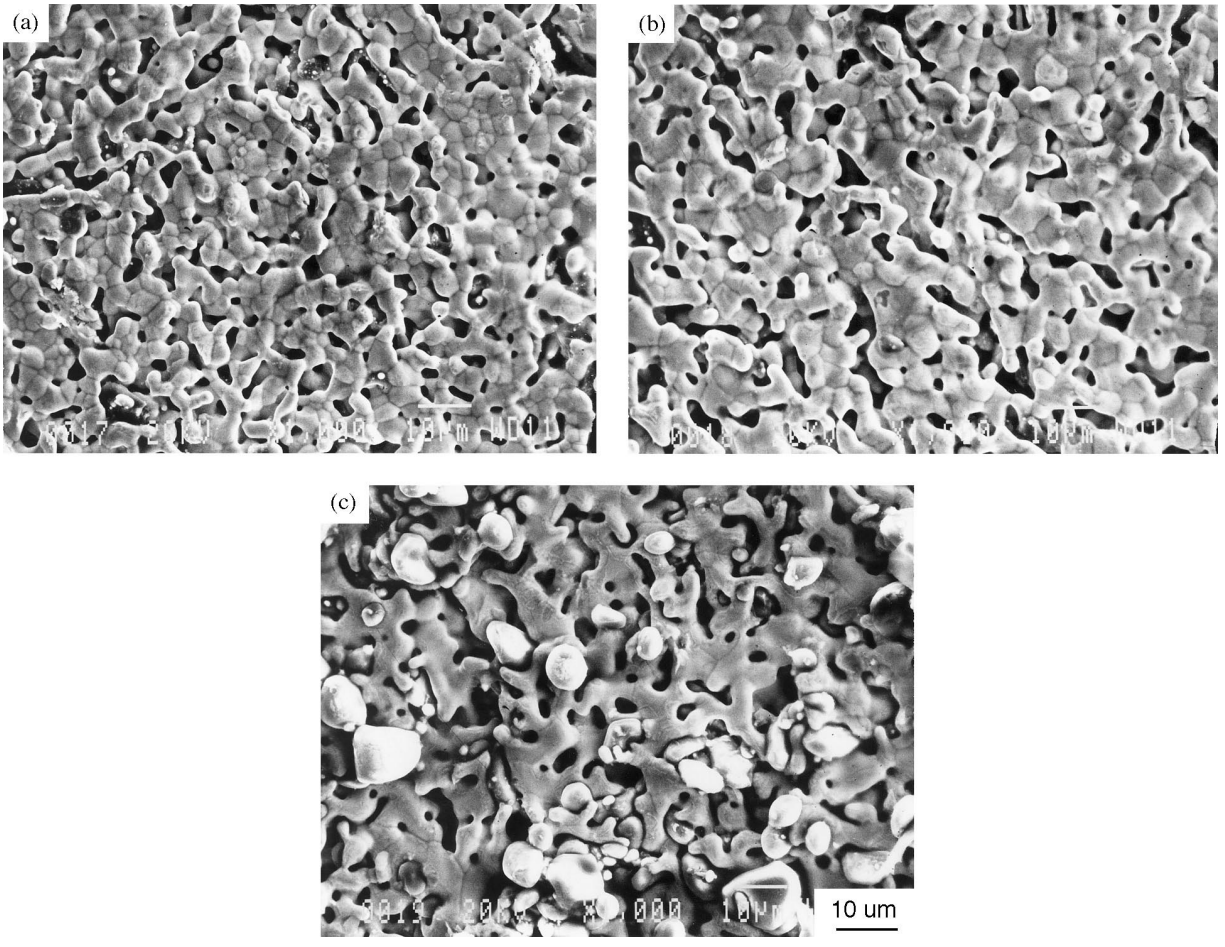

Fig. 5. SEM photographs of the surfaces of $MoSi_2 + 25$ vol% Al_2O_3 platelets composite as sintered at different temperatures: (a) 1650°C, (b) 1700°C and (c) 1750°C.

$$MoSi_2 + \frac{5}{2}O_2 \rightarrow MoO_3 + 2SiO \quad (4)$$

The free energy changes (values obtained from Knacke et al. [9]) of Eq. (4) at 1650, 1700 and 1750°C were −151, −152 and −153 kcal mol^{-1}, respectively. The negative free energy change indicated that Eq. (4) was thermodynamically favorable during sintering at these temperatures and both MoO_3 and SiO of these reaction products were volatile, so that large weight losses occurred during sintering. This weight loss was reflected by an increase in porosity in the samples that were put on the third layer as shown in Fig. 5, which would significantly reduce the relative density of the sample. Fig. 5(c) showed that a number of Al_2O_3 platelets were left on the surfaces of samples sintered at 1750°C because of the oxidation of $MoSi_2$. Maloy et al. [10] also found that large weight losses had occurred during hot pressing at 1800°C in $MoSi_2$ + C alloys containing 2 and 4 wt% carbon. The weight losses were as high as 20 and 47% in these two alloys, respectively. They thought that carbon must be necessary for such active oxidation, perhaps in some catalytic mode or by lowering the oxygen partial pressure in the hot pressing atmosphere. But the weight losses still occurred in the carbonless composites in this paper. The principle impurities of $MoSi_2$ powders and Al_2O_3 platelets were shown in Table 1.

It is very interesting that the sintering behaviors of the samples on different layers are so different in such a small crucible. The highest relative density can be obtained in the samples on the third layer at both 1650 and 1700°C, but the weight loss is the highest at the same time. It can be easily understood that the weight loss is the highest for the samples on the third layer because of less Al_2O_3 powders cover, but it will be discussed further whether the highest relative density and weight loss resulted from the temperature gradient in the crucible. This indicates that a higher relative density can be obtained if a more closed crucible is used or a theoretical density of 5.69 g/cm^3 cannot be used to calculate the relative density of the sample at this time because a large weight loss results in the obvious change in the sample compositions. The results shown in Table 7 and Fig. 5(c) indicate that 1750°C is too high to sinter $MoSi_2 + Al_2O_3$ platelets composite.

4. Conclusions

1. The particle size of $MoSi_2$ powders can be refined by attrition milling. The as-received $MoSi_2$ powders with a mean diameter of 2.57 μm were refined to a mean diameter of 0.56 μm by attrition milling for 72 h.
2. A higher green density of $MoSi_2 + Al_2O_3$ platelets composite powders mixtures can be obtained by mixing $MoSi_2$ powders with different particle sizes. The green density can be more improved by adding finer $MoSi_2$ powders to the $MoSi_2$ matrix. A maximum green relative density of 60.3% of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite mixture can be obtained by adding 50 vol% milling 72 h $MoSi_2$ powders into the $MoSi_2$ matrix. The further increment of the refined $MoSi_2$ powders leads, on the other hand, to a decrease in the green relative density.
3. A large weight loss occurred during sintering which evidently reduced the relative density of $MoSi_2$ + 25 vol% Al_2O_3 platelets composite; 88.6% of relative density of this composite can be obtained by pressurelessly sintering the billets with the highest green relative density of 60.3% at 1700°C×2 h. The sintering behaviors are very different for the samples on the different layers even in a small closed crucible.

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