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High-pressure sintering of bulk MoSi₂: Microstructural, physical properties and mechanical behavior



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ABSTRACT

In this study, using MoSi₂ powder as starting material, the bulk MoSi₂ samples were sintered at 1000–1600 °C under 5.5 GPa in a DS6 \times 14MN cubic press. Furthermore, their sintering behavior and mechanical properties were investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM) and indentation tests. XRD results elucidate that MoSi₂ can still maintain its body-centered-tetragonal structure after the high pressure and high temperature (HPHT) sintering. SEM images imply the combination between grain growths and re-crystallization. Strong covalent bonding between the grains is crucial for improving the mechanical properties of samples. But re-crystallization results in a large number of pores between grains in the sintered body, so that the density and hardness was reduced. Indentation tests indicate that sintered MoSi₂ have hardness values of 13.6–15.0 GPa, which increase with increasing temperature and is harder than polycrystalline and single crystal MoSi₂. The results demonstrate that the sintered MoSi₂ at 5.5 GPa/1300 °C possesses outstanding mechanical properties, including a high relative density (6.23 g/cm³), Vickers hardness (15.0 GPa) and fracture toughness (10.7 MPa m^{1/2}) at applied load of 29.4 N. In addition, the oxidation resistance of the prepared samples is measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. The results show that the oxidation resistance has been significantly improved from this work compared with polycrystalline MoSi₂.

1. Introduction

New materials are used under high temperature have been developed recently. Especially nickel aluminides, titanium aluminides, transition metal boride and transition metal disilicides have been intensively investigated as a high-temperature architectural material [1,2]. The transition metal disilicides are of great interest because they have been found to possess superior physical and chemical properties such as high hardness, high melting point and oxidation resistance, and have widely used in range of industrial applications [3–8].

Molybdenum disilicide (MoSi₂) is a borderline ceramic-intermetallic compound with double characteristics as being like metal and ceramic as well, which offers high melting point (2300 K), moderate density (6.24 g/cm³), elevated oxidation resistance (about 1600 °C), relatively lower coefficient of thermal expansion (8.1×10^{-6} K⁻¹) and high thermal conductivity (25 W/m K) [9]. Such unique properties give MoSi₂ materials a wide application area such as advanced engineering ceramics (high temperature heating elements, high temperature antioxidant

coatings, wear-resistant parts, diesel engine glow plug) [10]. In particular, MoSi₂ hybrid composite materials will be used as candidate materials for turbine engine components, such as turbine blades, combustion chambers, and nozzles [11]. In recent years, many studies have demonstrated that MoSi2 was an excellent reinforcement/sinteradditive in developing TiB₂, ZrB₂, HfB₂, TiC, TaC, HfC, ZrC, Si₃N₄ etc. materials for high-temperature applications, and improving their fracture toughness, density, and oxidation-resistant property [12-16]. Unfortunately, its practical applications are limited by three problems in industry: poor toughness at ambient temperature, poor creep strength at elevated temperature [17,18] and suffering from accelerated oxidation at low temperatures (about 400-600 °C) which was first discovered by Fitzer [19] in 1955 and was named pest oxidation. Its low toughness may partly result from the intrinsic difficulties of dislocation movement caused by a special $C_{11b}\xspace$ crystal structure, and the brittle grain boundary of SiO₂ glass phase formed by oxygen contamination in the preparation process [20]. In addition, the oxygen contamination in the

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preparation process which leads to the low relative density of MoSi2 ceramics. Oxidation material which is loose, porous, discontinuous and filmed with low relative density accelerates oxygen diffusion and leads to aggravation of the oxidation. On the contrary, the high relative density material forms a compact and continuous oxide film. The mass gain is less because of the hindering the diffusion of oxygen [21]. Therefore, many researchers have been devoted to improvement of the mechanical properties of MoSi2 ceramics in material design and preparing technique since the early 1970s [22]. In material design, adding the second phase, such as Nb, Mo, W, ZrO₂, SiC, Si₃N₄, TiB₂, Al₂O₃, La_2O_3 , Mo_5Si_3 et al. [23–26], to enhance the properties of the matrix, was usually viewed as a major method. MoSi2 is an abundant, relatively low-cost material which is non-toxic and environmentally friendly. therefore MoSi2 and MoSi2-based materials be regarded as the second nickel-based super alloy of a new class of highly competitive hightemperature structural materials [27].

Although MoSi2 and its composites have been used in industrial applications, especially high temperature heating devices and high temperature oxidation coatings, the scope of application is still limited compared with its immense application potential. With the rapid development of powder metallurgy technology and composite technology, the preparation technology of MoSi2 and its composites has made great progress. Since the 1980s, mechanical alloying (MA), self propagating high temperature synthesis (SHS), hot isostatic pressing (HIP), solid state displacement reaction and in situ reaction synthesis are widely used in the preparation of MoSi2 materials [28,29]. These methods overcome the shortcomings of traditional processes so the MoSi2 ceramics has high melting point, difficult synthesis and easy oxidation in the process of material synthesis. However, all the above production routes are pressure less or low pressure sintering (< 0.5 GPa). It is difficult to prepare high-relative density MoSi2 of sintered material used above methods.

For MoSi2 and MoSi2-based materials to be successful in elevatedtemperature structural applications, it is necessary to improve hightemperature strength and creep resistance, as well as low-temperature fracture toughness. In this study, in order to get better performance of MoSi₂ ceramics, HPHT sintering is adopted in the sintering of MoSi₂ bulk materials. Previous study shown that the HPHT method can sufficiently improve relative density of materials, prevent the growth of grain in the sintered compacts, promote plastic deformation and the close voids between MoSi2 grains, which would not have been obtainable by an ordinary mechanical mixing technique [30]. Compared to the conventional mixture method, the high pressure method is favorable for improving the mechanical properties. This work present a detailed study on the HPHT preparation and investigation of the physical properties and mechanical behavior of bulk MoSi2 materials such as microstructural characterization, relative density, fracture toughness and oxidation resistance. This study thus contributes to the design of new high temperature refractory composite materials through providing a practical guideline by considering multiple combined factors that may influence their performance in Mo-Si systems.

2. Experimental procedures and calculation methods

2.1. Specimen preparation

Initial powder (fine grain size $1 - 3\mu$ m, > 99.8% purity) purchased commercially from Alfa Aesar was used as starting materials in the present study. The initial powder was subjected to high energy ball milling to obtain more grain defects and small size particles. 20 g of MoSi₂ powders were sealed in a tempering steel vial, and milled for 50 h under a high-purity argon atmosphere, with 10 mL n-hexane as a process control agent. The ball to powder weight ratio was 10:1. Then the sample was loaded in molybdenum (Mo) capsules every 1.8 g, and dried in vacuum furnace (~ 1.5×10^{-3} Pa and 1000 °C) for 2 h in order to remove the oxygen and get rid of impurity gases attached to the grain surface and remaining organic matter. After vacuum furnace treatment, the powder was pre-compressed (about 600 MPa) into thick discs (11.0 mm in diameter and 4.5 mm in height) with a relative density of about 68%. The HPHT synthesis experiments were carried out in DS6 \times 14MN cubic press.

The sample assembly for the HPHT sintering experiments is shown in Fig. 1a. The pyrophyllite (32.6 mm in side length) was used as the pressure-transmitting medium to provide relative hydrostatic pressure. The closed dolomite tube (16.8 mm in diameter and 21 mm in height) was used as insulating materials. The closed cylindrical graphite tube was used for heating. The steel ring was used as a conductive electrode. The pre-pressed specimen was surrounded by a tube of NaCl pressure medium which could provide specimen with a relative hydrostatic pressure environment. The cell temperature was measured directly with PtRh6%-PtRh30% thermocouple, the pressure was calibrated by means of the known pressure-induced phase transitions of the standard metals Bi, Tl and Ba at room temperature. Detailed experimental procedures can be found elsewhere [31]. The preload sample starting materials were sintered at high pressure (5.5 GPa), high temperature (1000-1600 °C with intervals of 100 °C) for 30 min. During the HPHT sintering, the all specimens were first compressed to 5.5 GPa and followed by heated to the desired temperature with a heating rate of 150 °C/min. In order to make sure the heating more uniformly, we maintained the process for 30 min when the temperature reached the highest temperature value. After the samples were quenched to room temperature with cooling rates of about 100 °C/min and then decompressed to ambient pressure. At last, the samples were soaked in nitrohydrochloric acid 2 h so that the wrapped molybdenum was removed. Fig. 1b shows the HPHT sintering curve of the sample which set the highest temperature at 1600 °C. The cylindrical products with a diameter of about 10 mm and thickness of about 4.5 mm are shown in Fig. 1c.

2.2. Sample characterization

The sintered samples were characterized by x-ray diffraction (XRD, model DX-2500, Dandong, China) using a Cu-Ka radiation source with $\lambda = 1.5404$ Å to check the crystal structure, purity, morphology and phase identification. Scanning electron microscopy (SEM; JSM-6490, JEOL, Akishima, Japan) with an accelerating voltage of 200 kV was performed on the polished surface and fracture surfaces to detect the microstructure of the samples. In addition, the impressions and cracks of the indents were further characterized by SEM. The densities of the sintered bodies were obtained by Archimedes method.

The Vickers hardness (Model FV-700, Future-Tech., Japan) was performed with an applied load of 29.4 N with a time of 15 s on polished surfaces. Vickers hardness of samples was calculated using [32]:

$$H_{\nu} = 1.8544 \frac{P}{d^2}$$
(1)

where P is the load on the plane, and d is the impression diagonal average.

The fracture toughness (K_{IC}) was calculated qualitatively by indentation fracture technique under 29.4 N indentation load. The following expression for indentation fracture toughness was used for the present calculations [33]:

$$K_{IC} = A(\frac{E}{H})^{1/2} \frac{P}{c^{3/2}}$$
(2)

where A is a constant with a value of 0.016, c is the average of the four surface radial crack length (μ m). *E* and *H* are the elastic modulus (440 GPa [34]) for MoSi₂ and Vickers hardness (H_{ν}) values (GPa).

The sintered body was cut into the thick discs with 2 mm in diameter and 1 mm in height, in order to test its thermal stability. Differential scanning calorimetry analysis (DSC, TG-Q600, TG-Q2000, USA) was carried out to test ranged from 26 °C to 1400 °C at 10 °C/min in an air atmosphere to determine the oxidation resistance of the samples.



Fig. 1. (a) Sample assembly for HPHT sintering experiment: (1) pyrophyllite, (2) dolomite, (3) graphite furnace, (4) NaCl, (5) Mo sheet, (6) steel ring, (7) starting powder and (8) molybdenum wrapped; (b) HPHT sintering curve of MoSi₂; (c) sintered specimens.

3. Results and discussion

3.1. X-ray diffraction phase analysis

As shown in Fig. 2a, the x-ray phase identification results and SEM images (Fig. 3a) of starting powder indicate that the starting samples have a good crystallinity and morphology, and a small number of a metastable phase of Mo₅Si₃ with tetragonal structure exists. Fig. 2b shows the XRD patterns of samples sintered at different temperatures for 30 min at 5.5 GPa. As can be seen from Fig. 2b, with higher temperature, there are always two phases of MoSi2 and Mo5Si3 in all the specimens, and the content does not change. The full width at halfmaximum (FWHM) of the (103) peak of MoSi2 and devitatoric strain of sintered body are calculated as a function of the sintering temperature. Fig. 2c shows that the sample sintered at 1300 °C exhibits a maximum devitatoric strain, and the corresponding (103) peak (Fig. 2d) become asymmetric, which probably indicates that the microstructural defects and refined grains resulted from the HPHT treatment [35,36]. For the higher sintering temperature, the line-width continues to narrow. These special microstructures may be able to improve the hardness, strength and mechanical properties of sintered samples.

3.2. Microstructural characterization

In order to trace this regular development and gain more insight, several scanning electron microscopy (SEM) experiments were conducted. From Fig. 3a-b shows that the sample particles after vacuum treatment maintain in the starting powder size, and the grains are uneven distribution and have no grain growth. Fig. 3c-f shows the SEM images of fracture surfaces of samples sintered at 1000-1600 °C under 5.5 GPa. At the lower sintering temperature (Fig. 3c), no obvious grain growth was observed. With temperature increasing to 1300 °C (Fig. 3d), the impression that particle boundaries are not well bonded is confirmed by the clean separation at particle interfaces, resulting in most intergranular fracture which is evidence of good bonding among particles which might contribute to the hardness and fracture toughness. With temperature increasing 1400 °C, transgranular fracture (arrows in Fig. 3e) occurred which resulting in decreased mechanical properties. With a further increase in temperature to 1600 °C, not only transgranular fracture appeared (Fig. 3f), the original grain boundaries of the sample also start to disappear as an evidence of grain growth which was responsible for the decrease in hardness. This can also be confirmed by

the fracture toughness of the sintered sample, as shown in Fig. 5.

It can be seen from Figs. 3c and 4a that a lot of the pores be found between grains in the sintered sample and the fine-grained particle fraction aggregations were usually localized in coarse-grain joints, indicating that the present sintering temperature is not high enough to realize the metal-cermet combination between the adjacent MoSi₂ particles. As can be seen from Fig. 4a mechanical connections are found between most of the grains, and the interfacial bonding between grains was not obvious. With the increment of sintering temperature, the deformations of the MoSi₂ particles occurred more easily and the contact areas of coarse grain may be enlarged, accompanied by the closing of the pores. High temperature also can promote grain growth and bonding among particles. At a higher sintering temperature (1300 °C), from Figs. 3d and 4b, physical bonding between grains was observed, thus a higher density could be achieved, and the sample of ideal performance be obtained. Compared with the Figs. 3c and 4a, its grain boundary is significant reduction, which indicates that the interface is well bonded. Ultra-high pressure can eliminate pores at modest temperature, promote bonding among particles with increasing temperature (Fig. 4a-b) but failed to inhibit abnormal grain growth and nonuniform crystallites at grain boundaries at higher temperature (Fig. 4c-d). So, the transparency of sintered samples first increases and then shows an obvious decrease with increasing temperature. With the temperature increasing to 1400 °C, grain boundary is difficult to distinguish, but simultaneously with abnormal grain growth and pores growth are shown in Figs. 3e and 4c. This phenomenon also can be found elsewhere [37,38]. When the sintering temperature is higher than 1400 °C, the sintered samples re-crystallized, presented in Figs. 3f and 4d. Excessive temperatures cause the interface energy to be too large, grain boundaries through the pores, the pores were wrapped in the grain inside. Owing to the pores are separated by the grain boundaries, they can not be removed from grain boundaries that are a fast passage, so that the density is not increased.

3.3. Density

In this work, a series of sintering experiments under different temperatures (1000–1600 °C) were conducted under 5.5 GPa for 30 min. High density of specimens was obtained and shown in Fig. 5. The traditional preparation method is difficult to enhance the density of the $MoSi_2$ sintered body. However, HPHT sintering can effectively improve the material density and reduce the porosity of the material. It can be



Fig. 2. (a) The x-ray diffraction patterns of starting specimen under normal pressure and room temperature; (b) Samples sintered under various temperatures at pressures of 5.5 GPa. The club represents the diffraction peak of $MoSi_2$ and the spades represents the diffraction peak of MoS_5Si_3 ; (c) FWHM of (111) x-ray line and devitatoric strain of $MoSi_2$ as a function of sintering temperature; (d) Amplified peak of (103) $MoSi_2$.

seen from Fig. 5 that the highest relative density is 99.7% (6.23 g/cm^3) at 1300 °C. If the temperature is below 1300 °C, the density and volume collapse rate of samples are increased with the temperature rising, when the sintering temperature exceeds 1300 °C, the density and volume collapse rate of samples are decreased obviously. The physical properties of samples such hardness and high temperature oxidation resistance may be improved by increasing its relative density.

3.4. Vickers hardness and fracture toughness

The Vickers hardness and fracture toughness of the sintered sample was measured with a standard square-pyramidal diamond indenter using loads of typically 29.4 N with the hold time of 15 s. The loads were deliberately chosen, in order to allow the measurement of fracture toughness at different places where microstructures showed variations throughout the materials, and most importantly to allow fracture toughness measurements to be made under conditions where errors were incurred due to the onset of significant radial crack length. But high loads will cause the measured value of hardness is small compared to the actual value. The hardness values and fracture toughness of samples were deduced from the average of about 10 indentations to minimize errors, and the standard deviation values are estimated as about 2% and 2%. This fully illustrates that the overall performance of the sintered body prepared by the HPHT method is relatively homogeneous. Compared with the traditional preparation method, the samples prepared by HPHT sintering have a high hardness and fracture toughness, which increase with the fabrication temperature rises up to 1300 °C. However, the fracture toughness increases with increasing

temperature continues to 1500 °C. With increasing sintering temperature, the closure of pores and bonding among particle boundaries might be contribute to the obvious improvement of hardness. Abnormal grain growth and pores growth are responsible for the decrease of microhardness at higher temperature which is in agreement with the results of microstructures and density changes. This has been demonstrated in a number of studies that showed one reason can be advanced for its low toughness: the brittle grain-boundary SiO₂ phase, which typically forms as a consequence of oxygen contamination [39]. The sintered material by the HPHT method effectively prevent a SiO_2 phase formed, thus improved the fracture toughness of the material. The MoSi₂ sintered has a high hardness of 15.0 ± 0.3 GPa and fracture toughness of 10.7 ± 0.2 MPa m^{1/2} at 5.5 GPa/1300 °C. Variations in the Vickers hardness of the samples that were sintered at different temperatures are shown in Fig. 6a. The room temperature Vickers hardness and fracture toughness of polycrystalline MoSi₂ is 9.4 GPa and 3.0 MPa $m^{1/2}$ [40]. As can be seen from Fig. 6b, Vickers indentation and surface radial crack are very obvious. This can confirm the accuracy of our measurement methods and experiment results. This value is similar to that of a polycrystalline, Si₃N₄ ceramic material which is densified without the use of densification aids. It is found from Table 1, Figs. 5 and 6a show that the density affects the hardness of the sintered samples, and the greater the density, the higher the hardness at 1300 °C. The density and hardness changes are also in agreement with the microstructure observations presented in Fig. 4.



Fig. 3. SEM images. (a) Starting powder; (b) Starting powder dried in vacuum furnace (~ 1.5 × 10⁻³Pa and 1000 °C) for 2 h; Fracture surfaces of samples sintered at: (c) 5.5 GPa/1000 °C, (d) 5.5 GPa/1300 °C, (e) 5.5 GPa/1400 °C and (f) 5.5 GPa/1600 °C.

3.5. Oxidation resistance

The thermal stability of the MoSi₂ samples sintered at 1000 °C, 1300 °C and 1600 °C at 5.5 GPa are shown in Fig. 7. The Mo₅Si₃ additions to MoSi₂ tended to be detrimental to oxidation properties has been

intensively investigated [47]. To the sintered samples at 5.5 GPa/ 1000 °C, both an endothermic peak (580 °C) and an exothermic peak (1280 °C) in DSC curves appear due to it is susceptible to a "pest oxidation" reaction which causes catastrophic disintegration by a combination of oxidation and fracture in the intermediate temperature range



Fig. 4. SEM micrographs of corroded polished surface of samples sintered at: (a) 5.5 GPa/1000 °C; (b) 5.5 GPa/1300 °C; (c) 5.5 GPa/100 °C; (d) 5.5 GPa/1600 °C.



Fig. 5. Relative density and volume collapse of sintered bodies at pressures of 5.5 GPa for 30 min as a function temperature.

between 400 °C and 600 °C, and accompanied by a 2% loss of quality [48]. The loss of mass may be attributed to the volatilization of MoO_3 that was generated by the $MoSi_2$ oxidation reaction. When the temperature reaches 1280 °C, MoO_3 is completely volatilized and the heat flow of the sample is not changing. Sharif et. al [49] analyzed the

oxidation mechanism from the thermodynamic point of view. The reaction equation is as follows:

$$2\text{MoSi}_2(s) + 7\text{O}_2(g) \rightarrow 2\text{MoO}_3(s) + 4\text{SiO}_2$$
(3)

$$2Mo_5Si_3(s) + 21O_2(g) \rightarrow 10MoO_3(s) + 6Si_2$$
 (4)

However, when the sintering temperature is higher than 1300 °C, nearly the both TGA and DSC curves tends to level. The thermal stability of the sintered sample at 5.5 GPa/1300 °C is better than that of the sintered sample at 5.5 GPa/1600 °C. Previous studies have indicated that the occurrence of pesting may depend on the presence of cracks or porosity in prepared material, on pores in samples made from powder, or on the alloy composition (silicon versus molybdenum-rich) [42]. Alloys with lower silicon, including the compound Mo_5Si_3 , have been shown to be more susceptible to pesting [50]. The results revealed that the $MOSi_2$ sintered body of high density and high purity contribute to improve oxidation resistance and restrain effectively "pest oxidation". The bulk materials of $MOSi_2$ prepared by the HPHT method possess good oxidation resistance (Higher than 1400 °C) that is better than that of most metals and ceramic-based composites.

4. Conclusions

In summary, the bulk $MoSi_2$ was sintered at high pressure and a relatively moderate temperature (5.5 GPa/1300 °C) by using mixed size



Fig. 6. (a) The Vickers hardness and fracture toughness of the samples sintered at 5.5 GPa with an applied load of 29.4 N as a temperature function. The green inset: optical photo of Vickers indentation; (b) SEM micrographs of Vickers indentation at 1300 °C.

Table 1			
Vickers hardness (Hv), fracture toughness (K _{IC}) and relative densi	ty data of MoSi2, SiC,	TiB ₂ , Si ₃ N ₄ and MoSi ₂ .	based composites.

Materials	Hv (GPa)	<i>K_{IC}</i> (MPa m ^{1/2})	Load (N)	Relative density (%)	Preparation technology	Ref.
Polycrystalline MoSi ₂	9.4	3.1	29.4	~ 97	HIP/SHS	[40]
Single-crystals MoSi ₂	8.0		9.8			[41]
SiC	27.1	3.6	9.8			[42]
TiB ₂	24.4	3.2	49	~ 97.8	HTHP	[43]
Polycrystalline Si ₃ N ₄	19.0	9.8	9.8	~ 97.5	HPS	[44]
(20 vol%) ZrO ₂ -MoSi ₂	10.6	4.5	29.4	~ 95.5	HIP	[24]
(20 vol%) SiC-MoSi ₂	11.6	4.4	88.2	~ 98.5	Hot-pressed	[25]
(20 vol%) TiB ₂ -MoSi ₂	10.6	5.1	9.8	~ 98	Vacuum plasma spraying	[45]
MoSi ₂ -Metal (10–20 vol% Nb, W, Mo, B, Al)	8-14.2	> 11	49	~ 97.5	HIP/MA	[46]
Monolithic MoSi ₂	15.0	10.7	29.4	99.7	HPHT	This work



Fig. 7. TG-DSC curves of the samples sintered at 1000 $^\circ\text{C}$, 1300 $^\circ\text{C}$ and 1600 $^\circ\text{C}$ under 5.5 GPa.

 $MoSi_2$ powder as the starting material. The observations on microstructure, density and hardness reveal that the high compactness positively affected the sintered samples. The sample has a homogeneous dense structure with $MoSi_2$ grain contact directly. Results show that the products obtained via HPHT sintering have high density (6.23 g/cm³), high hardness (15.0 GPa) and high fracture toughness (10.7 MPa m^{1/2}), which are significantly higher than that of products obtained through conventional sintering method, even higher than single crystal $MOSi_2$ (8.0 GPa). It is important to highlight that "pest oxidation" at low temperature (400–600 °C) is suppressed at HPHT by increasing the density and purity of sintered body $MOSi_2$. The affordable starting material and eco-friendly experimental conditions could allow for promising future applications of $MOSi_2$.

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