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Formation and Reaction Kinetics of Mo and Mo Silicides in the Preparation of $MoSi_2/SiC$ Composites

Wen-Cheng Wei* and J. S. Lee

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 106

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Abstract

Mo/Si/SiC composite powder was first prepared by a process combining dissolution-precipitation, spray-drying and hydrogen reduction steps. The powder was then hot-pressed at the temperatures ≥1400°C to form $MoSi_2/SiC$ composites. The analysis on the phase reactions of Mo/Si/SiC, grain growth kinetics of Mo grains, and the transformation kinetics of Mo_5Si_3 and $MoSi_2$ phases during and after H_2 reduction was completed by quantitative XRD technique. In addition, the powders and hot-pressed composites were characterized by SEM, TEM, and HRTEM, appeared virtuous properties of uniform chemical composition and fine grains. The mechanical properties, including flexure strength, hardness, and toughness of some densified composites, are reported and compared to the properties of pure $MoSi_2$ and SiC. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

SiC and $MoSi_2$ are two high temperature materials, and have several electric and oxidation properties in common. They are often used as the materials for making heating element and are thermally stable if making the $SiC/MoSi_2$ composite.[1] The SiC and $MoSi_2$ are two major crystalline phases in the molybdenum–silicon–carbon ternary phase diagram which includes molybdenum silicides (Mo_xSi_y), silicon carbide (SiC), molybdenum carbide (Mo_2C) and the intermediate phases.[1,2] These crystalline phases have the similar characters that are high in melting temperature and good in electric conductive property. The last two systems are often classified as ceramics, used in structural and heating applications at high temperature. The first material system (Mo_xSi_y) belongs to intermetallic compound, representing Mo_3Si, Mo_5Si_3 and $MoSi_2$. These three compounds perform resistant to oxidation similar to SiC. In addition, the properties of metallic conductivity and high temperature plasticity of these silicides are occasionally reported.[3] Among these, molybdenum disilicide ($MoSi_2$) is the most widely used material for heating element in furnaces with operation temperature up to 1800°C.

Polycrystalline $MoSi_2$ is one of good electric conductive material at high temperature and behave a transition of mechanical properties from 'brittle to ductile' at the temperature between 900 to 1000°C. The plasticity of the silicide at high temperature is resulted from the formation and movement of dislocations.[4,5] The $MoSi_2$ behaves 2% strain before failure in a 1300°C creep test. That would increase toughness, but reduce yielding strength of the silicide at high temperature.

SiC is a structural and electronic ceramic material, and has a wider application than $MoSi_2$. Due to a strong covalent bond between Si and C, the bonding nature of SiC materials ensure its high hardness, and is especially beneficial on the property of wear resistance. In addition, good oxidation resistance and semi-conductive properties of SiC have granted its performance as a heating element at high temperature, but only up to 1550°C.

Low toughness and hard to sintering of SiC and $MoSi_2$ are two foreseen problems, and prohibit the uses in stringent applications, e.g. engine parts, which need several excellent properties at high temperature. Toughness improvement of pure SiC and $MoSi_2$ has been the topic of several research works. For instance, Sasaki[6] reported the preparation

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*To whom correspondence should be addressed.

of pressureless sintered SiC from β-phase powder and demonstrated the formation of elongated α-grains in the densified matrix. The densified SiC performed a better toughness due to an interlocked microstructure. However, the improvement is rather limiting. On the other hand, the addition of sintering aids, for instance alumina or yttria, can form a liquid phase at grain boundary so to enhance the densification of SiC. Although these liquid phase can transform to crystalline phases (e.g. Y–Al–garnet) as it is cooled from sintering temperature, the structural properties at high temperature are still restricted.

Essentially, SiC and $MoSi_2$ are two thermally stable phases in the Mo–Si–C phase diagram at 1600°C, and could co-existing with Mo_5Si_3C or Si.[1] Therefore, the research in the past reported several attempts to improve the mechanical properties of $MoSi_2$ by addition of different types of SiC, for instance, Carter *et al.*[7] using SiC particulate or Gac *et al.*[8] and Bose *et al.*[9] using SiC whisker. The purpose of SiC incorporated into $MoSi_2$ is designed for the utilization of their stability at high temperature in atmosphere and for the combination of their merits, good strength of SiC and good plasticity of $MoSi_2$ at high temperature. Gac and Petrovic[8] have reported that SiC-whisker-reinforced $MoSi_2$ are indeed improved in toughness ($8{\cdot}2\,\mathrm{MPa}\sqrt{\mathrm{m}}$) and yielding strength (four times better) than a pure $MoSi_2$.

The SiC/$MoSi_2$ composites can be synthesized by directly hot-pressing of SiC and $MoSi_2$ powders[10] or by the reaction sintering of other types of powders. The density of the composites[10] with 10 vol% SiC and the sintering additives, e.g. boron, alumina or yttria, is poor ($<90\%$) even hot-pressed at 1950 to 2050°C. The other researches[11,12] used the mixture of Mo, Si and C powders as the precursors. They found[11] that the silicide was formed above 1342°C, and the composites with 10 vol% or more of SiC could not be pressureless-densified at 1550°C unless hot-pressed at a higher pressure. Hanager *et al.*[13] reported a different route that used the reaction and sintering of Mo_2C with Si at 1200°C or higher temperature. The densified composites hot-pressed at 1350°C for 2 h followed by 1 h at 1700°C resulted in preferred-oriented SiC platy grains along reaction direction. Hanager *et al.* also depicted that the grain size of SiC and $MoSi_2$ in the composite could be controlled in micrometric size by using hot pressing of Mo_2C and Si at 1700°C. The densification temperature is greatly reduced by using reaction sintering step.

Previous research reports[7–13] are almost concentrating on $MoSi_2$-based composites with SiC as an additive in the amounts less than 40 vol%. This work was planed to use MoO_3, Si and SiC precursors and to select SiC as the substrate material. Due to the advantages offered by the processing step of chemical route, the sizes of Mo and $MoSi_2$ grains are greatly reduced. In addition, the distribution of $MoSi_2$ in SiC substrate is optimized and shows great improvement in the densified microstructure.

2 Experimental Procedures

The precursors of the $MoSi_2$/SiC composites are molybdenum oxide (MoO_3, Climax Molybdenum Company, USA), Si (4E, KemaNord, Sweden) and SiC (UF-15, Lonza, Germany) powders. The detail physical and chemical properties of the powders are shown in Table 1. The MoO_3 which was in the state of aggregates of sub-micrometric particles was firstly dissolved in 5 wt% ammonia water to form a saturated ammonium molybdate solution. The Si and SiC powders were added in pure water and turbo-mixed for 1 h with zirconia grinding media to form second suspension. Two suspensions were then mixed in a specified quantity so to form compositions with the $MoSi_2$/SiC volumetric ratio from 10/90 to 50/50. The samples are designated as S90, S80, S70 or S50 which represents the volumetric percentage of SiC.

The suspensions with solid loadings varied from 5 to 20 vol% were ball-milled for 1 h and passed through a 150-mesh screen. After degassing and vibrating continuously for a few minutes in a vacuum chamber, then were subjected to spray drying (BUCHI 190 spraying drier, BUCHI, Switzerland). The mixture was continuously stirring during spray-drying. The spray-drying conditions were set as follow: liquid flowing rate 400 ml min^{-1}, hot-air flowing rate 600 N1 h^{-1}, inlet temperature 160 to 200°C, outlet temperature 90 to 100°C. For operational convenience and the prevention of the evaporation of ammonia, the suspension

Table 1. Properties of the powders used for the preparation of $MoSi_2$/SiC composites

Property	*SiC (UF-15)*	*MoO_3*	*Si (4E)*
Specific surface area ($\mathrm{m}^2\,\mathrm{gm}^{-1}$)	15	—	3·5
Medium grain size	0·6	2^a	3·7
Crystalline phase[b]	6H(major)	Orthorhombic	Cubic
Purity	97%	99·95	99·8
Major impurity (>100 ppm)	C: 5000	None	C: 1000
	Si: 700		Al: 800
	Al: 200		Fe: 400
	Fe: 150		Ca:100
Theoretical density ($\mathrm{g\,cm}^{-3}$)	3·217	4·692	2·33

[a] The size is measured from SEM micrograph.

[b] Phases are verified by an X-ray diffractometer (PW1792, Philips Co., The Netherlands).

for spray-drying was maintained at 25°C. Therefore, Mo-species, Si and SiC loadings were concentrate enough for efficient spray-drying. The composite powders were then subjected to a hydrogen reduction furnace which was operated in a flow rate of H_2 gas 1 l min^{-1}, to the temperatures 400 to 1000°C for 0.25 to 4 h. After the reduction of molybdate phase, the powder in same quantity were die-pressed by a uniaxial pressure of 85 MPa to disk shape in a diameter 25 mm. The disks then were treated at higher temperatures 1100 to 1350°C in a graphite furnace (Jen-Hwa Co., ROC) venting with Ar (99·95% pure), H_2 gas or operated in vacuum condition.

The reduced powder, which was first hydrogen-reduced at 900°C for 2 h, then was hot-pressed in a graphite furnace (High-multi 500, Fujidempa Kogyo Co., Ltd., Japan) operated in a vacuum atmosphere of 1×10^{-4} torr. The conditions of hot-pressing were as follow: ramped from room temperature to 1100°C in a rate of 20°C min^{-1}, then changed to 5°C min^{-1} to 1350°C, stayed for 2 h until the formation of $MoSi_2$ was complete. Then raised the furnace temperature to hot-pressing temperature (1400 to 2000°C) in a rate of 5°C min^{-1}. The composites were sintered for 1 h at the peak temperature and a pressure 25 MPa, then cooled down in the furnace. For comparison, a pure SiC sample doped with 2 wt% of alumina (A-16SG, Alcoa Co., USA) was hot-pressed at 2000°C in the same heating schedule.

Physical properties of the spray-dried powder of various formulation were characterized by different analysis methods. Observation of the morphologies of spray-dried powder was conducted by using a SEM (JSM-T100, JEOL Co. Ltd., Japan). The SEM specimens were prepared by drying a droplet of alcoholic suspension with the spray-dried powder on the top of a carbon-painted aluminum stage. The homogeneity of composite powder was evaluated with the similar procedure as our previous paper.[14] X-ray diffractometer (Philips PW1710, Philips Co., The Netherlands) with a slow scanning rate of 0·005° 2θ s^{-1} was used to do the quantification of six crystalline phases. The diffraction parameters and sources of the phases used for the standards are listed in Table 2. Scherrer equation was used to estimate the crystalline sizes of Mo, Si and SiC. The relationship of the FWHM (full width at half maximum) of the diffraction peaks to the measured grain size of Mo phase in ceramics[14] was the basis for the estimation of Mo and Si in $MoSi_2/SiC$ composites. The constant k in Scherrer equation was adapted from our previous report[14] on the Mo/Al_2O_3 composite system.

Interfacial microstructure and chemical composition were analyzed by a high resolution transmission electron microscopy (FETEM HF-2000, Hitachi Co., Japan). The $MoSi_2$ and $MosSi_3$ grains in the hot-pressed composite were used as the standard for the calibration of X-ray adsorption coefficient of Mo and Si. Therefore, the Mo/Si ratio of each microstructure features, including glassy phase, in the composites can be quantified. The ceramographic observation of polished composites was conducted on SEM (Philips 515, Philips Co., The Netherlands) equipped with X-ray energy dispersive spectroscopy (EDS).

Test bars in the dimensions $4 \times 3 \times 36\,mm^3$ for the fracture strength test of the hot-pressed composites, as well as SiC (S98A2) and $MoSi_2$ sample (cut from Super 33 heating elements, Kanthal Co., UK) were carefully prepared followed previous report.[15] The test conditions were following the procedures specified by JIS 1601 standard. Density and porosity measurement were conducted according to ASTM 372-73. Due to the porosity, only four hot-pressed composites, S70 and S50, SiC and $MoSi_2$ were polished and tested by a hardness tester (MVK-EII, Akashi Co., Japan) with an indentation load 1·0 kgf and lasted for 15 s. Two fully densified samples, S50 and $MoSi_2$, were tested by a Vicker's micro-indentor with a load 10 kg.The toughness was calculated followed the equation given by Evans.[16]

3 Results and Discussion

3.1 Phase evolution of composite powders

Two spray-dried powders were analyzed by XRD, one was aged for 2 days, the other was aged for 50 days after spray-dried. Besides Si and SiC phases, XRD patterns reveals that a broaden peak between 10 and 14° 2θ, representing an amorphous

Table 2. Diffraction parameters for quantitative XRD analysis of various Mo–Si–C powders

Composition and purity (%)	*Phase*	*(hkl)*	2θ (degree) of (hkl)	*Scanning range*	*Supplier*
SiC (97%)	6H	(006)	35·656	35·15–36·15	Lonza, Germany
Mo (99·8%)	Cubic	(110)	40·510	40·00–41·00	Climax Special Metals, USA
Si (99·8%)	Cubic	(111)	28·448	27·95–28·95	KemaNord, Sweden
$MoSi_2$ (99·5%)	Tetragonal	(103)	44·833	44·35–45·35	Aldrich Chemical, USA
Mo_5Si_3 (99%)	Tetragonal	(411)	42·760	42·25–43·25	Johnson Matthey, USA
Mo_2C (99%)	Hexagonal	(101)	39·492	39·00–40·00	Johnson Matthey, USA

phase of molybdate for the sample in short aging time. However, the amorphous molybdate would transform to crystalline $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ phase[17] if aging for 50 days at ambient temperature.

The hydrated molybdate phase in S70 sample was analyzed by TGA from room temperature to 500°C. The reaction is shown below

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \rightarrow 7MoO_3 + 6NH_4OH + H_2O \quad (1)$$

The maximum weight loss of the sample was 7.6% which was very close to the theoretical value (7·88 wt%) of the decomposition loss of hydrated molybdate in the S70 sample.

The as-spray-dried powder could be reduced by hydrogen gas from 400 to 1000°C. Figure 1 is the diagram illustrating the crystalline phases appeared in the powder of an ammonium molybdate/Si/SiC composition (S70) treated at various temperatures and durations. The XRD results reveal that the hydrate transforms to MoO_2 at the temperature above 400°C, then to Mo phase starting from 600°C and completing ca 700°C.

To control the reduction of Mo oxide is very important to keep the composition stoichiometric.[18] MoO_3 is sublimating above 795°C, and the loss of Mo may result in a composition rich in Si. Therefore, either Si, Mo_5Si_3, or $Mo_{\leq 5}Si_3C_{\leq 1}$ would stay with $MoSi_2$ and SiC in the composite if any of MoO_3 was left after incomplete hydrogen reduction treatment.

The Mo phase remains with SiC and Si until the temperature reaching 1000°C, and results in Mo_2C and Mo_5Si_3 phases. The reactions can be

$$2Mo + SiC \rightarrow Mo_2C + Si \quad (2)$$

and

$$11Mo + 3SiC \rightarrow Mo_5Si_3 + 3Mo_2C \quad (3)$$

Previous reports[19,20] have conducted a series of analysis on the interfaces of reacted Mo/SiC treated from room temperature to 1200°C. Hara *et al.*[19] have found the formation of Mo_2C is keeping in front of Mo_5Si_3 phase. They concluded that the diffusivity of carbon in Mo is faster than Si in Mo. Similar results are also confirmed by Gaib *et al.*[20] However, the formation of Mo–Si compound is found as low as at room temperature in high vacuum condition, but no report on the type of the Mo–Si phase.

For a short reaction time (15 min), the results of crystalline phases of the composite powder in Fig. 1 indicate that eqn (2) is dominating. The changes of Mo, SiC and Si were also investigated by quantitative XRD, and shown in Table 3. The formation of Mo_2C in eqn (2) is company with the decrease of SiC and the increment of Si. However, the amount of Si decreases as the reaction proceeds to 1 h at 1000°C (Table 3, third condition). The trend shown in Table 3 is consistent to the prediction of eqn (2).

Figure 2 is the X-ray diffraction patterns of the composites powders treated above 1100°C and in various atmosphere conditions, either in H_2, Ar or vacuum. The phases found after 1100 or 1200°C

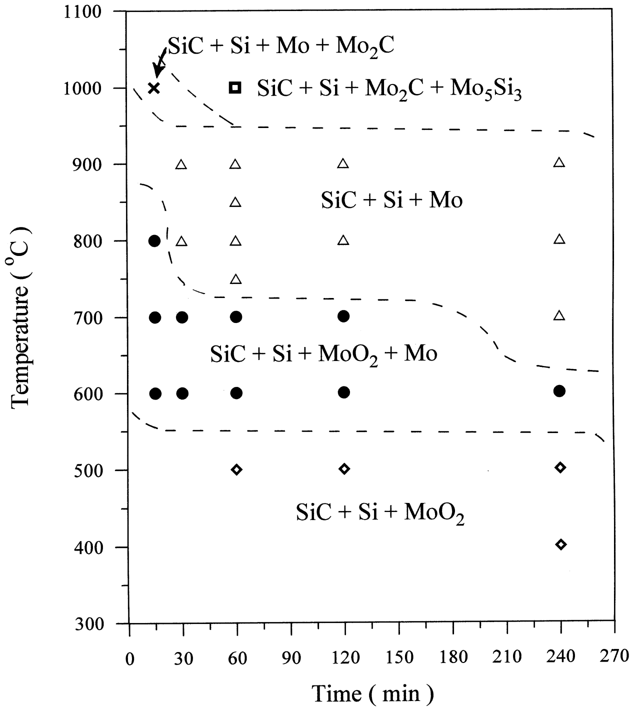

Fig. 1. Treatment temperature versus duration for the reaction products of ammonium molybdate/Si/SiC powder in H_2 atmosphere.

Table 3. Quantitative XRD analysis on three S70M30 composition shown in Fig. 1

	SiC	*Si*	*Mo*	*Mo_2C*	*Mo_5Si_3*
800°C–1 h	63·5 vol%	25·9 vol%	10·6 vol%	0 vol%	0 vol%
1000°C–0.25 h	61·3 vol%	26·8 vol%	9·8 vol%	2 vol%	0 vol%
1000°C–1 h	59·6 vol%	20·4 vol%	0 vol%	5·6 vol%	14·4 vol%

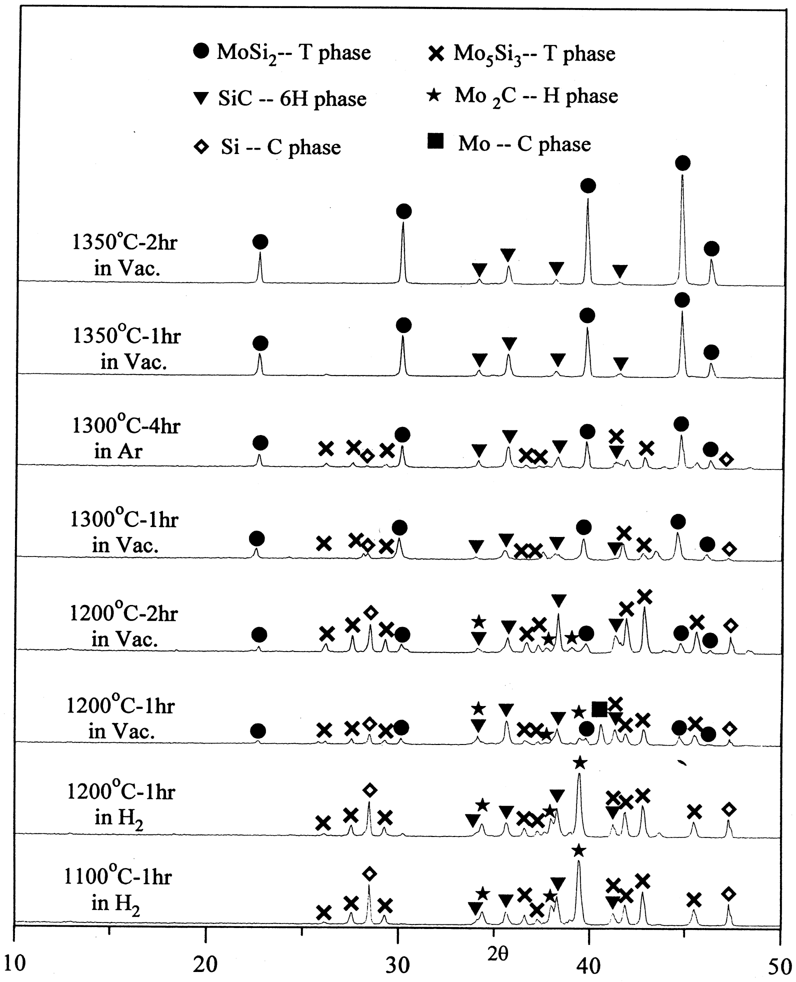

Fig. 2. X-ray diffraction patterns of S70 powders treated by different atmospheres from 1100 to 1350°C for 1 to 4 h.

treatments in H_2 are the same as the one obtained at 1000°C (Fig. 1). But the $MoSi_2$ is starting formed in vacuum at 1200°C or higher temperature. At higher temperature, there are only two pure phases, SiC and $MoSi_2$ are observed on the XRD patterns for the samples calcined at 1350°C for 2 h in vacuum.

The phases shown in Fig. 2 are quantified and reported in Table 4. It is apparent that vacuum condition for the calcination is beneficial to the first appearance of $MoSi_2$ phase, see the S50 and S70 cases that in vacuum at 1200°C. In addition, operation in vacuum, e.g. the S50 case 1 h at 1300°C, is also better than that in Ar, e.g. S70 operated 4 h at 1300°C. The amount of $MoSi_2$ of 1 h treatment at 1300°C is 26.1 vol% in vacuum, but only 18.7 vol% in the sample has been treated for 4 h in Ar atmosphere. Therefore, the treatment conditions that a hydrogen reduction operated at 900°C and the calcination at 1350°C for 2 h in vacuum were selected for the preparation of composite powders used in the following hot-pressing operation.

Two phases formed between 1100 and 1350°C, i.e. $MoSi_2$ and Mo_5Si_3 are quantitative analyzed and reported in Fig. 3 and Table 4. The formation rate of $MoSi_2$ is nearly linear, and can be fitted by the broken lines drawing from the origin of Fig. 3. Three formulations of the composites, S70, S80 and S90 (containing 70 to 90 vol% of SiC), show the similar reaction behavior that the formation of $MoSi_2$ is proceeding by consuming Mo_5Si_3. It may represent a simple first-order reaction for the following transformation:

Table 4. Quantitative results of $MoSi_2$ and Mo_5Si_3 phases in Mo/Si/SiC heat-treated at 1100 to 1350°C

Sample	*Treatment*	*Mo (vol%)*	*Si (vol%)*	*SiC (vol%)*	*Mo_2C (vol%)*	*Mo_5Si_3 (vol%)*	*$MoSi_2$(vol%)*
S50	1100°C—1 h H_2	0	29·7	34·7	10·3	25·3	0
	1200°C—1 h H_2	0	30·4	35·7	10·1	23·8	0
	1200°C—2 h vacuum	0	24·1	40·1	0·7	30·5	4·6
	1300°C—1 h vacuum	0	5·7	42·6	0	25·6	26·1
	1350°C—2 h vacuum	0	0	48·5	0	0	51·5
S70	1200°C—1 h vacuum	2·5	9·3	68·0	2·2	14·5	3·4
	1300°C—4 h Ar	0	1·6	69·2	0	10·5	18·7
	1350°C—1 h vacuum	0	0	69·0	0	5	16·5

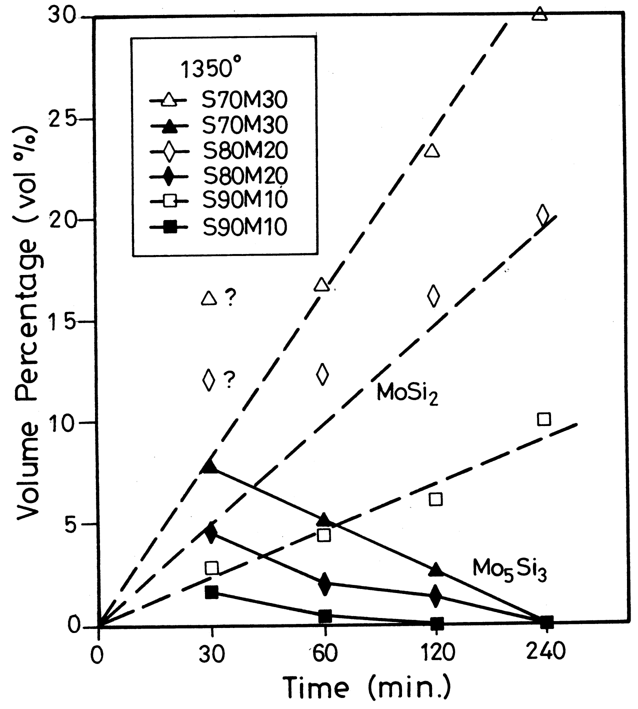

Fig. 3. X-ray quantitative analysis results of $MoSi_2$ and Mo_5Si_3 phases

$$Mo_5Si_3 + 7Si \rightarrow 5MoSi_2 \qquad (4)$$

The equation shows that the reaction of one mole of Mo_5Si_3 needs 7 moles of Si. The quantification data depicted in Table 4 do not show any Si left after the treatment at 1350°C for 1 h in vacuum conditions. The source of Si and the reaction path are not known if interpreted only from the QXRD data. That might be a Si-containing glassy phase formed in the composite but invisible in XRD pattern. Later, a detail microstructure analysis will be presented to resolve the query.

Figure 4 is a typical XRD pattern of a $MoSi_2$/SiC composite hot-pressed at temperature above 1800°C. There are three phases found in the hot-pressed composites, 6H-phase SiC, T-phase $MoSi_2$ and a minor 4H-phase SiC. No other carbide or silicide phase is identified. It seems no carbide, silicide, glassy phase and SiO_2 were identified by the XRD technique. However, the reaction sintering of Mo, Si and C powder reported by Alman *et al.*[11] that often produces an Mo_5Si_3C minor phase due to the presence of silica, and the reaction is hard to control due to an exothermic reaction of silicides. A detail analysis on the microstructure was conducted using analytical TEM and HRTEM, and would be reported later.

3.2 Formation and grain growth of Mo in SiC/Si matrix

The as-spray-dried composite powder was treated with hydrogen gas. The morphologies of the powders before and after hydrogen reduction are shown in Fig. 5. Large flaky crystals appear [Fig. 5(a)] on the surface of spray-dried granules. These flaky molybdate crystals, fine SiC and Si particles are found on the dried granules which are in the sizes from 3 to 15 μm. It is the typical sizes for the agglomerated granules formed by a laboratorical spray drier. The flaky crystals disappear as they are reduced at 900°C by hydrogen, as shown in Fig. 5(b). Fine powders, to be Mo, Si or SiC, are observed uniformly distributed on the surface of the as-H_2-reduced granules.

Figure 6(a) is the crystal size of Mo in Mo/Si/SiC composite powder treated at 600 to 1000°C for different durations. The size (G) of Mo increases slightly by obviously as the period of thermal treatment increases. The kinetics of the grain growth of Mo can be formulated as below

$$G = G_o + Kt^n \qquad (5)$$

where G_o is the initial size of Mo particles, K is a constant but is related to thermal activated process. The time exponent, n, can be obtained from the slopes of the curves in Fig. 6(a) which is plotted by taking a logarithmic scale. The inverse values $(1/n)$ of the slopes are estimated between 17·3 to 18·8. At present, no appropriate theory is proposed to explain the kinetics for the growth of Mo grains in Si/SiC matrix. The phenomena depict that the growth is concurrently occurring by the reduction of MoO_2 and the sintering of extremely fine Mo in hydrogen atmosphere. The transport of Mo gas molecule in H_2 and help the coarsening of Mo at the temperatures below than 1000°C cannot be ruled

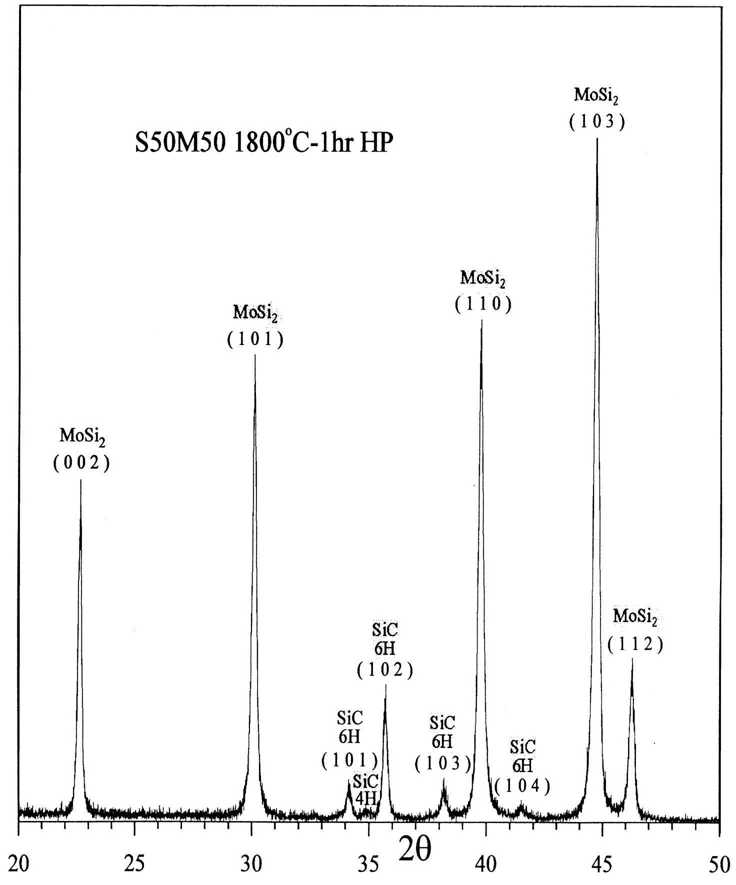

Fig. 4. X-ray diffraction pattern of S50 by hot-pressing at 1800°C and 25 MPa for 1 h.

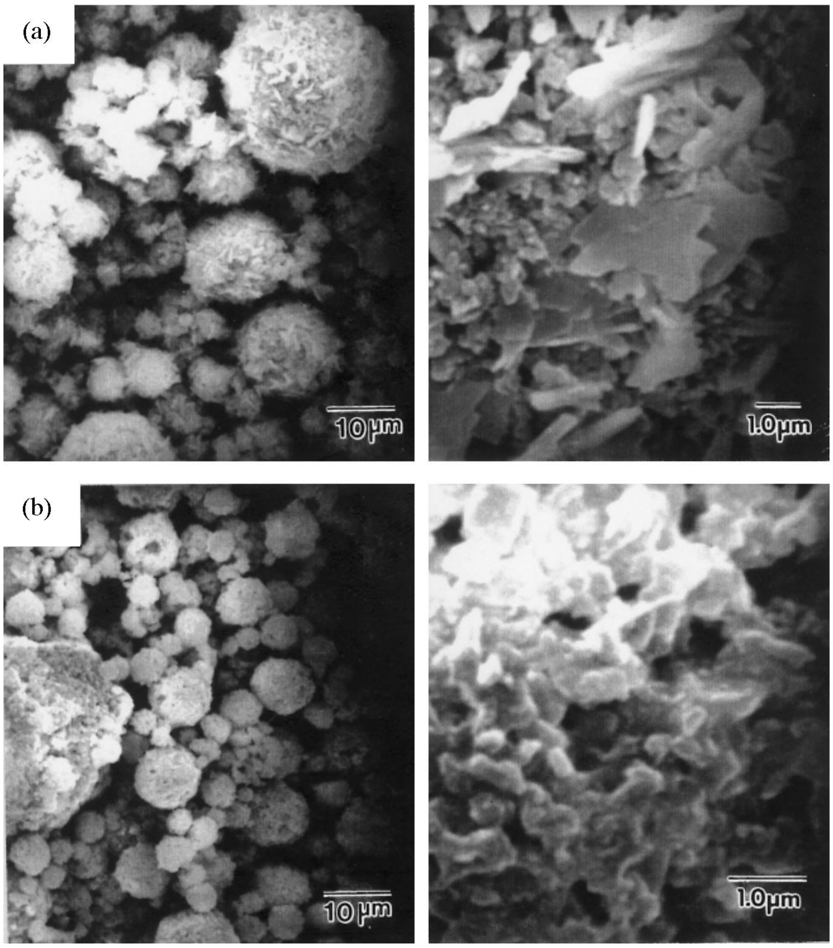

Fig. 5. SEM micrographs of (a) as-sprayed and (b) as-H_2-reduced powders in different magnifications.

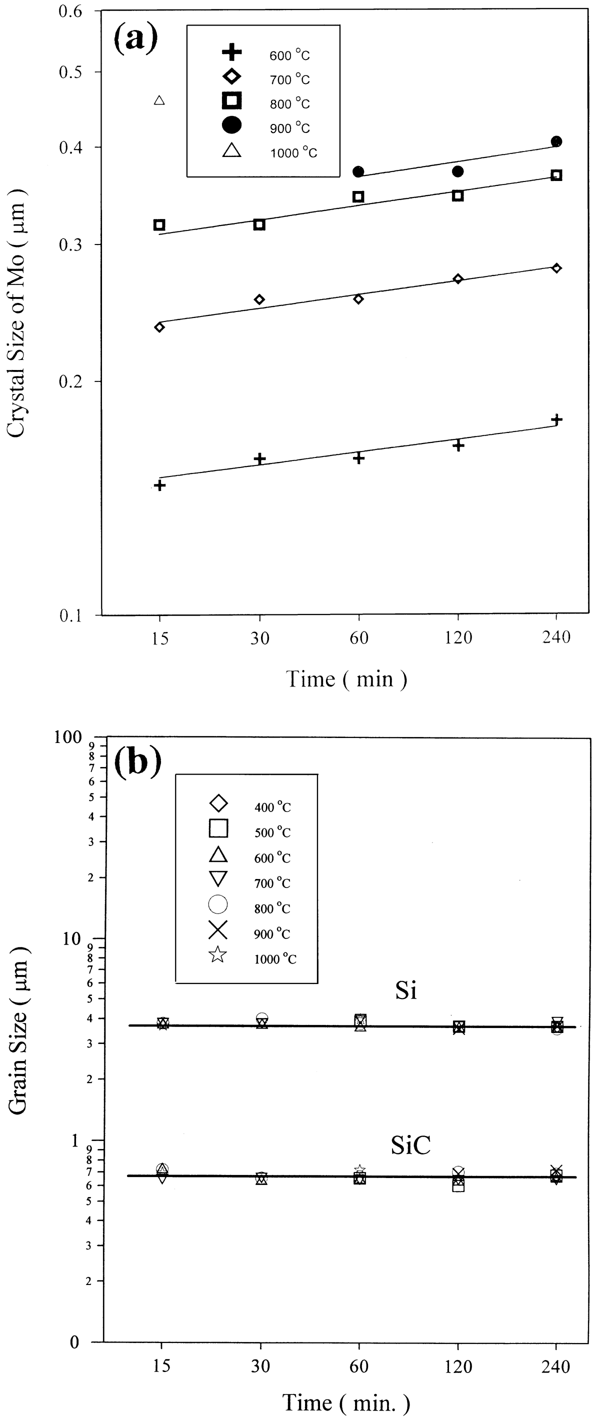

Fig. 6. Grain size of Mo in Mo/Si/SiC composite powder at 600 to 1000°C for various durations; (b) grain size of Si and SiC treated at 400 to 1000°C for various durations.

out due to the size of Mo to be far less than 0·1 μm. The sintering of Mo nano-particles is not ever reported in literature.

The crystalline sizes of Si and SiC treated at similar temperature region, 400 to 1000°C, are also reported in Fig. 6(b). The sizes of Si and SiC are 3·7 or 0·65 μm, respectively. The grains are hardly growing below 1000°C even treated as long as 4 h. Therefore, SiC and Si particles are stable at temperature below than 1000°C.

3.3 Properties of hot-pressed $MoSi_2$/SiC composite

Relative density of $MoSi_2$/SiC composites with $MoSi_2$ contents from 10 to 50 vol% is shown in Fig. 7. A density data of SiC sample (S98A2) with 2 wt% Al_2O_3 additive is also shown in the figure for comparison. The $MoSi_2$/SiC composites were hot-pressed at 1400 to 2000°C. The highest density of the composites can get is 100% T.D. of S50 at 1900°C; 95% T.D. of S70 at 1950°C; and 70% T.D. of S90 at 2000°C. The SiC (S98A2) without the addition of $MoSi_2$ can be fully densified at 2000°C. The beneficial role of $MoSi_2$ to the densification of SiC is obviously weaker than alumina, but still have some degree of positive enhancement on the densification, e.g. the case of S70 with 30 vol% $MoSi_2$.

Three dense $MoSi_2$/SiC composites in the series of S90, S70 and S50 are characterized by SEM and TEM. Figure 8 is the SEM micrographs in which $MoSi_2$ grains appear brighter features and SiC grains are in dark contrast. The grain sizes of both phases are seldom greater than 5 μm. The microstructure illustrates a porous character of S90 composite [Fig. 8(a)] which shows 30% porosity. The other hand, two denser composites, S70 [Fig. 8(b)] and S50 [Fig. 8(c)], exhibit a uniform distribution of $MoSi_2$ and SiC.

There are glassy phases occasionally found at the grain boundary or multiple-grain positions in the composites, especially these hot-pressed at 1900°C or higher temperatures. Figure 9(a) shows a high resolution lattice image of a molybdenum silicide

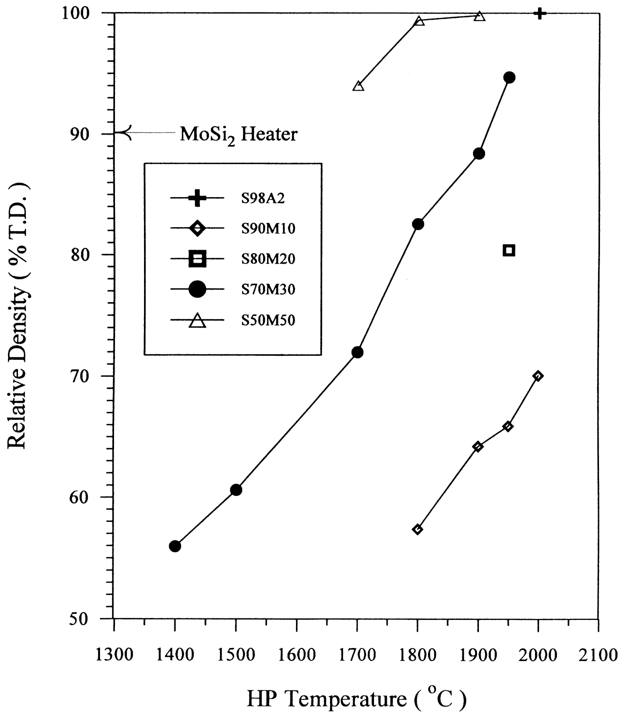

Fig. 7. Relative density of $MoSi_2$/SiC composites with various $MoSi_2$ contents. The composites were hot-pressed at different temperatures for 1 h

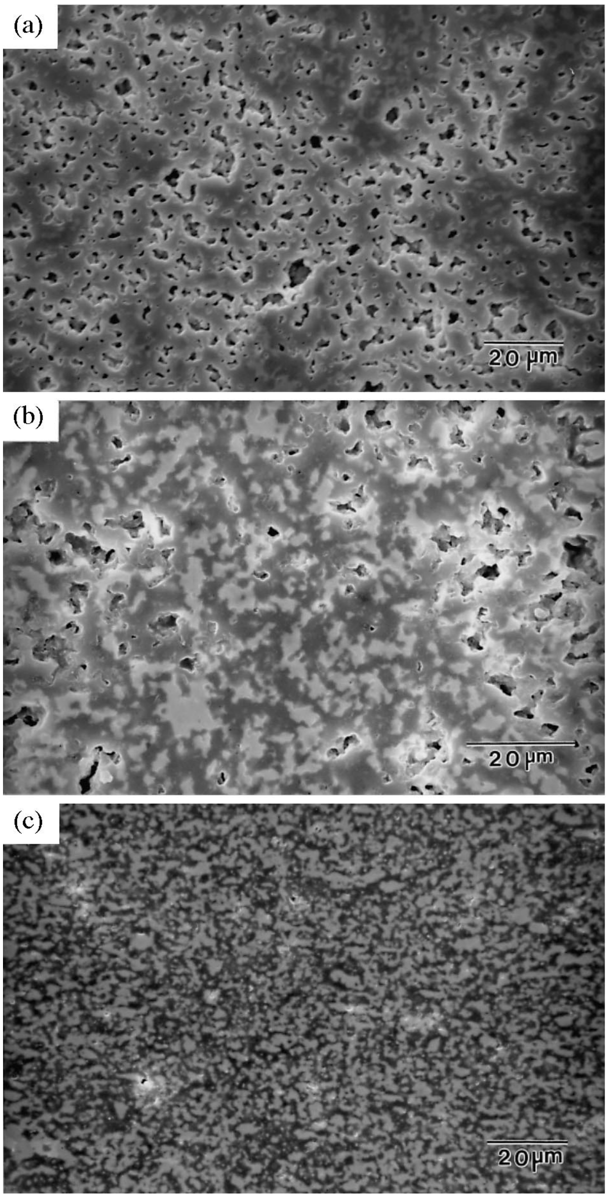

Fig. 8. SEM micrographs of hot-pressed $MoSi_2/SiC$ composites: (a) S90 at 2000°C; (b) S70 at 1950°C; (c) S50 at 1800°C for 1 h.

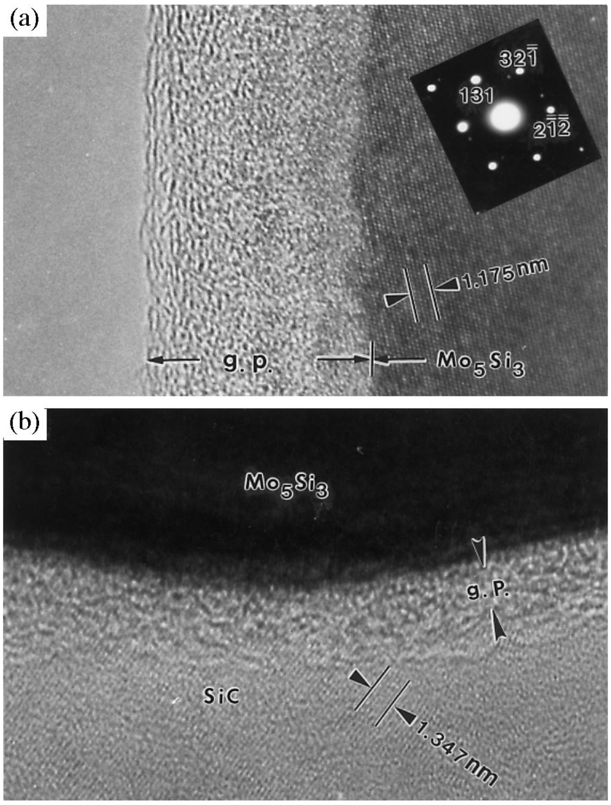

Fig. 9. High resolution lattice images of (a) Mo_5Si_3 with a insert of diffraction pattern and a glassy thin edge; (b) Mo_5Si_3/SiC interface illustrating a glassy boundary (g.p.) in a thickness of 3 nm. The S50 composites was hot-pressed at 1900°C for 1 h.

near the edge of thin foil. According to the inserted electron diffraction pattern (DP), the grain is an Mo_5Si_3 phase. An amorphous layer [marked 'g.p.' in Fig. 9(a)] in a width of 12 to 15 nm is observed. This amorphous layer is formed due to a readily oxidation of ultra-thin Mo_5Si_3 specimen (TEM specimen). However, the width is several folds larger than the thickness (ca 3 nm) of the glassy layer found at the Mo_5Si_3/SiC interface [Fig. 9(b)], and also larger than the thickness of the glassy boundary at the $MoSi_2$/SiC interface. Figure 10(b) shows a bright field TEM micrograph of S50 composite. The 'g.p.' region at the center of the micrograph in a size ranging from 0·2 to 0·6 μm is identified by diffraction pattern to be an amorphous phase. Moreover, the composition of the glass region was analyzed with microbeam EDS. The results are illustrated in Fig. 10(b).

The EDS spectra of $MoSi_2$ [as the example in Fig. 10(a)] and Mo_5Si_3 grains which are used as the internal standards for the calibration of the composition of other grains. The molar ratio of Si/Mo of the glassy region in the inserted micrograph Fig. 10(b) is 82/13. The glassy phase is much rich in Si and with a composition located at the liquidus projection of 1600°C in Mo–Si–C phase diagram.[1] Also note the intensity of oxygen relative to the intensities of carbon, Mo and Si. The glassy phase is an oxycarbide glass and a metastable phase which may represent a transition state of glassy formation. At last, the Si-rich glass may supply the Si content for the formation of $MoSi_2$ by consuming Mo_5Si_3 [eqn (4)] at sintering temperature.

Figure 11 is results of the four-point bending strength of $MoSi_2$/SiC composites. The bending strength values show 250 MPa to 50 MPa, and are strongly depending upon the density of the $MoSi_2$/SiC composites. The data of pure $MoSi_2$ heater and SiC (S98A2) are included, which have a strength (ca 250 MPa) nearly equal to that of S70-1950 composite. It is noted that the sample S50-1800 with a density over than 99% T.D. shows a low strength of 165 MPa.

Hardness of four sets of samples were measured, including two $MoSi_2$/SiC composites, S70-1950 and S50-1800, one pure $MoSi_2$ heater and one

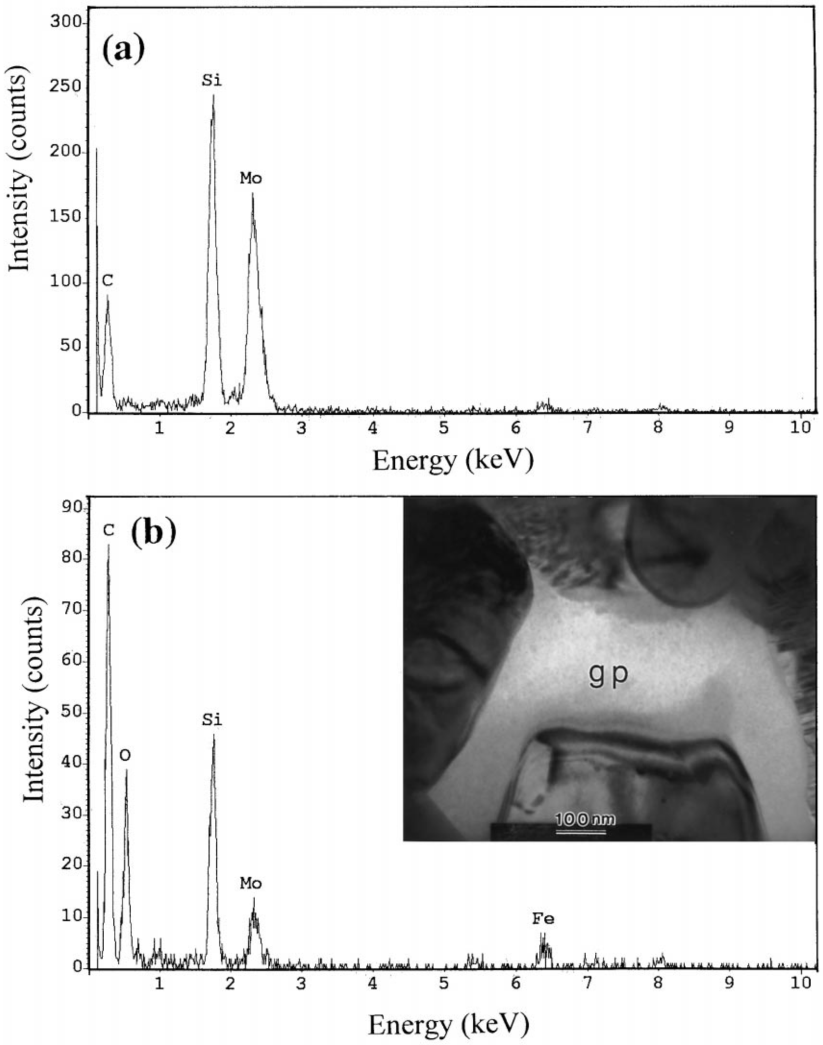

Fig. 10. EDS spectra of (a) $MoSi_2$ and (b) glassy phase. The inserted TEM bright field micrograph of an S50 composite illustrating the glassy phase (bright feature with a mark 'gp' at the center) surrounded by SiC and $MoSi_2$ grains. Note the intensity of iron in (b) is spurious that is resulted from ion milling during TEM sample preparation.

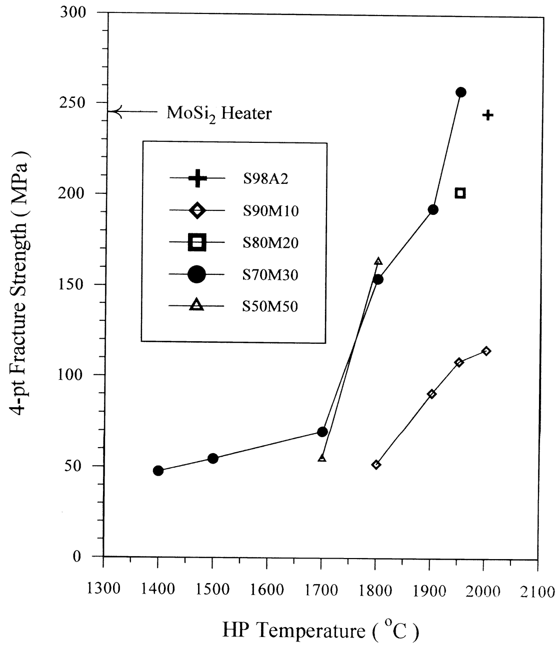

Fig. 11. Four-point bending strength of $MoSi_2$/SiC composites. The data of pure $MoSi_2$ heater and SiC (S98A2) are included.

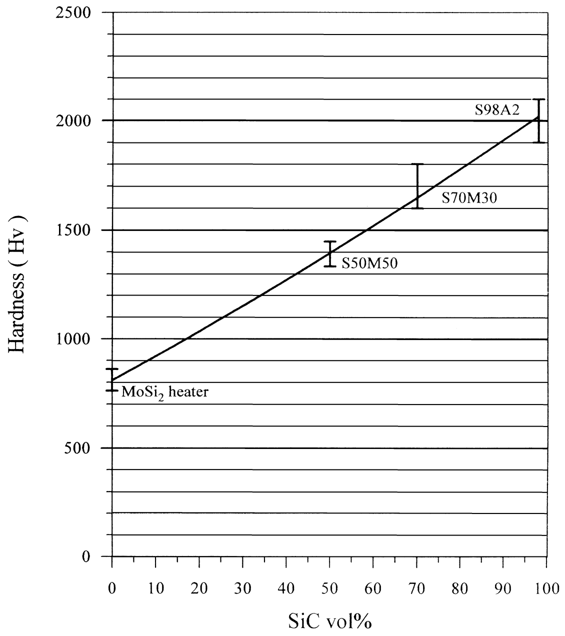

Fig. 12. Hardness of two $MoSi_2$/SiC composites, $MoSi_2$ heater and SiC (S98A2).

densified SiC (S98A2) sample. The results of the four samples are shown in Fig. 12 and the hardness is fallen between 2000 kg mm^{-2} (pure SiC) to 800 kg mm^{-2} (pure $MoSi_2$). The relationship of the hardness of the composites to the content of SiC is linear.

The toughness of S50-1800 and $MoSi_2$ heater was also determined by a micro-indentation technique. The toughness of these two samples is $3{\cdot}5\,MPa\sqrt{m}$ or $2{\cdot}3\,MPa\sqrt{m}$, respectively. The S50-1800 has a higher toughness than that of pure $MoSi_2$ heater.

4 Conclusion

The preparation procedures, including dissolution of molybdenum oxide in ammonium solution, colloidal dispersion of Si and SiC powders in molybdate solution, spray-drying of the suspension, hydrogen reduction and hot-pressing of the powder were used for the production of various $MoSi_2/SiC$ composites with a uniform and fine microstructure. The results can be concluded below.

1. Ammonium molybdate is reduced by pure hydrogen and transforms to Mo phase starting from 550°C. The formation of Mo can be completed at 700°C for 4 h or 750°C for 1 h. Then Mo grains are starting to react SiC, result in Mo_2C phase from 950°C. However, as the calcination temperature and time extended, Mo_5Si_3 and $MoSi_2$ are consecutive appearing until SiC and $MoSi_2$ are the two final phases if treated at 1350°C for 2 h in vacuum conditions.
2. The grain size of Mo grains prepared from the reduction of molybdate is between 0·1 to 0·4 μm. The kinetics of grain growth of the Mo is determined which shows the time exponent to be 1/18.
3. Vacuum condition, comparing to Ar or H_2 atmosphere, is beneficial to the first appearance of $MoSi_2$ phase. The $MoSi_2$ is formed starting from 1200°C.
4. The formation of $MoSi_2$ is taking place by consuming Mo_5Si_3 and Si content in glassy phase. The reaction is linearly proceeded as the calcination time prolongs at 1350°C.
5. S50, S70 are two composites can be densified by HP at 1900°C to a density greater than 95% T.D. The glass phase in a composition much rich in Si may help the sintering of $MoSi_2$ and SiC.
6. The distribution of $MoSi_2$ in SiC matrix is uniform. The sintered composites show grains sizes mostly less than 5 μm.
7. Hardness of the composites is fallen between the hardness of pure SiC and $MoSi_2$, and keeps linear relationship with the content of SiC.
8. The toughness of one $MoSi_2/SiC$ composite (S50) is $3{\cdot}5\,MPa\sqrt{m}$ which is higher than that ($2{\cdot}3\,MPa\sqrt{m}$) of an $MoSi_2$ heater.

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