

Effect of reactant composition on the production of MoSi₂ by self-propagating high-temperature synthesis

Sang Hwan Kim[†], Sang-Cheol Yeo and Gong Won Kang

Department of Chemical Engineering, Konkuk University, Seoul 143-701, Korea

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Abstract—The effect of reactant composition, particle size of silicon, density of powdered compacts, and reaction atmosphere on the characteristics of molybdenum disilicide produced from molybdenum and silicon powders by self-propagating high-temperature synthesis, was studied in a pressurized reaction chamber at 1.5 bar. The atomic ratio of silicon to molybdenum (Si/Mo) was changed from 1.0 to 2.6 in order to investigate the effect of reactant composition on the characteristics of self-propagating high-temperature synthesis. Stable combustion was observed for the values of atomic ratios of silicon to molybdenum from 1.8 to 2.2 and SHS-produced material consisted of a uniform and single-phased MoSi₂. In the meantime unstable combustion such as oscillatory, spinning, and surface combustion was detected for the values of atomic ratios of silicon to molybdenum less than 1.8 or larger than 2.2. SHS-produced material under unstable combustion includes the impurities of Mo₅Si₃, Mo₃Si, unreacted Mo and Si resulting from the layered or reacted-on-surface structures, which give lower degree of reaction and possibly poor electrical properties of heating element MoSi₂. The value of criterion α suggested by Shkadinskii et al. to differentiate stable combustion from unstable one, is found to be 0.74 for producing molybdenum disilicide by self-propagating high-temperature synthesis. Stable combustion was detected for the values of α greater than 0.74 ($\alpha > 0.74$) to give the uniform and single-phased product while unstable combustion was observed for the values of α less than 0.74 ($\alpha < 0.74$) to result in a non-uniform and multiphase product. This critical value will help the industry to produce uniform and high-purity molybdenum disilicide by self-propagating high-temperature synthesis processes.

Key words: Molybdenum Disilicide, Self-Propagating High-Temperature Synthesis, Stable Combustion, Spinning Combustion, Heating Element

INTRODUCTION

Self-propagating high-temperature synthesis is a new and innovative method for producing ceramic and metallic materials. In this method, a cylindrical sample consisting of compacted powder mixture is ignited at one end. The heat release from such exothermic combustion processes is sufficient to propagate the combustion wave through the sample and to completely convert the unburned reactants to products. Such reactions occur at temperatures above 2,000 °C, high enough to cause the evolution of most impurities existent in the reactants. At high reaction temperatures, the evolution process may be so violent that it can have deleterious effects on the structural integrity of the final ceramic products.

Conventional sintering method for producing refractory ceramics and intermetallics requires high-temperature furnaces and relatively long processing times. It is difficult to achieve and maintain high productivity. Moreover, solid-state reactions of powdered mixtures in high-temperature furnaces are often incomplete, allowing unreacted substances to act as impurities and leading to poor-quality products. When the reaction between metallic and non-metallic elements is highly exothermic, the heat liberated can sustain the reaction in the form of combustion waves which propagate until the reactants are converted to the products. This process pioneered by the Russians [1,2] has been extensively investigated in the United

States [3-7]. The SHS process has the advantages of shorter processing time, higher purity in the final products, and lower energy input.

Molybdenum disilicide produced by self-propagating high-temperature synthesis offers promise as a heating element in high-temperature furnaces because of its high melting temperature, excellent oxidation resistance, and mechanical strength. SHS-produced molybdenum disilicide at the end of the 1970s in Russia was reported to have the characteristics of the increased productivity, doubled service life, and improved performance.

The conditions for the formation of various silicides of transition metals by self-propagating high-temperature synthesis were discussed to synthesize the desired end products [8]. For the molybdenum-silicon, titanium-silicon, and zirconium-silicon systems, a study was made to investigate the effects of gaseous argon pressure ($p=3$ -150 bar), the diameter of compacts ($d=10$ -30 mm), the particle size of metal ($r=30$ -400 μm), and the ratio of reactants in the powder mixture on the combustion rate as well as the chemical composition of the combustion products. Metal-silicon systems turned out to make gasless combustion like the metal-carbon and the metal-boron systems and the combustion rate did not depend on the pressure of the inert gas. Combustion rates increased with the increasing diameter of powdered compacts and leveled off for a larger diameter greater than 20 mm for Mo+2Si systems.

The combustion characteristics of the molybdenum-silicon systems was studied both theoretically and experimentally [9]. The effect of average particle size of molybdenum and degree of product

[†]To whom correspondence should be addressed.

E-mail: sanghkim@konkuk.ac.kr

dilution on the combustion rates was investigated and the experimental results of combustion rates were in good agreement with those calculated by numerical method by using a one-dimensional model.

The molybdenum disilicide for the Mo+2Si system by sintering method at 1,100–1,550 °C was synthesized to investigate the physical and compositional properties of the products obtained in various conditions [10]. The MoSi₂ forming process starts at temperatures in the range of 1,100–1,300 °C. MoSi₂ synthesized at temperatures in the range of 1,300–1,400 °C contained the impurities of Mo₅Si₃ and MoSi_{0.65} in the final products. But the impurities of Mo₅Si₃ and MoSi_{0.65} were not detected in the larger quantities at temperatures above 1,400 °C. Therefore, MoSi₂ should be synthesized at temperatures higher than 1,500 °C for several hours.

In this paper, we attempt to investigate the effect of reactant composition, particle size of silicon, density of compact, initial temper-

ature, and reaction atmosphere on the characteristics of SHS-produced molybdenum disilicide and combustion wave propagation such as stable, oscillatory, and spinning combustions. The value of Shkadinskii's criterion α to differentiate stable from unstable combustion will be discussed in detail [11].

EXPERIMENT

The synthesis of molybdenum disilicide from the molybdenum and silicon powders was carried out in the following way as shown in Fig. 1. The molybdenum powder (99.96% pure), obtained from Hana Metal Company in Korea as –325 mesh, had an average particle size of 10 μ m. The silicon powder (99.90% pure), obtained from Shinyo Company in Japan as –325 mesh, had an average particle size of 18 μ m. We also used a silicon powder with the metallurgically lower purity (99.10% pure) to investigate the effect of silicon particle size on the characteristics of SHS-produced MoSi₂ and combustion wave obtained from Lucky Metal Company in Korea as shown in Table 1.

The well-mixed reactant powders after drying at 100 °C for 24 hr were pressed into cylindrical samples with diameter and height dimensions of 20 and 15–30 mm, respectively. The cylindrical samples were ignited in the pure argon gas at 1.5 bar as shown in Fig. 1. Ignition of cylindrical compacts was accomplished by heating the samples at one end by a resistively heated tungsten filament. Self-propagating high-temperature synthesis of molybdenum disilicide from silicon powder of different particle sizes and molybdenum was carried out in the reactor chamber at a pressure of 1.5 bar.

The reactant powders were analyzed for particle size, shape, and structure with a scanning electron microscope. Identification of reac-

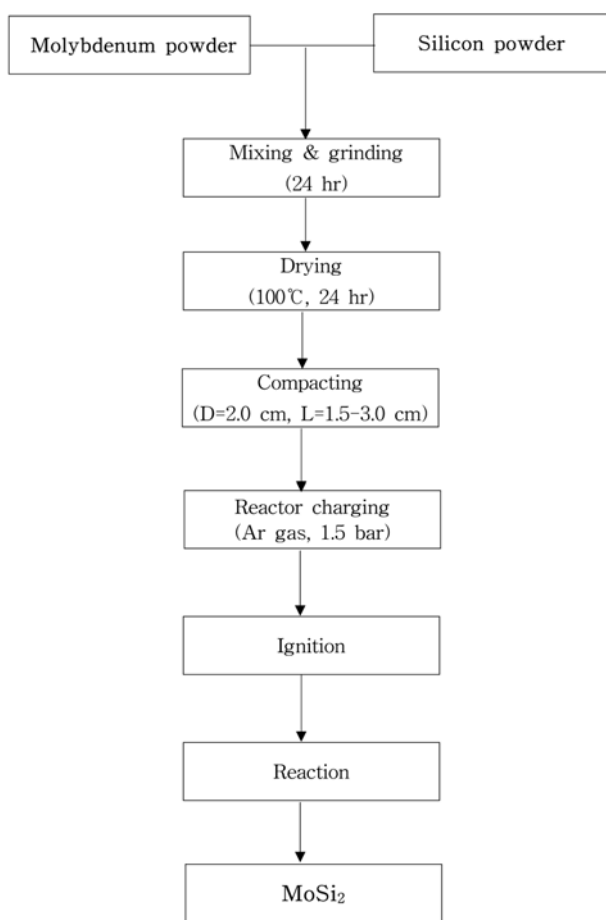


Fig. 1. Flowsheet for producing molybdenum disilicide by self-propagating high-temperature synthesis.

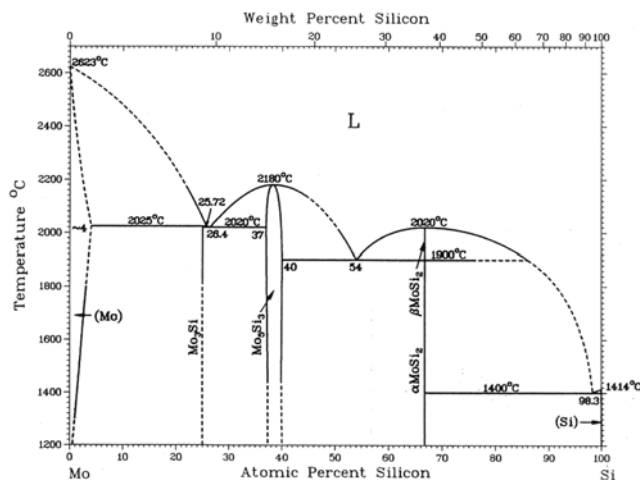


Fig. 2. Phase diagram of binary molybdenum-silicon systems.

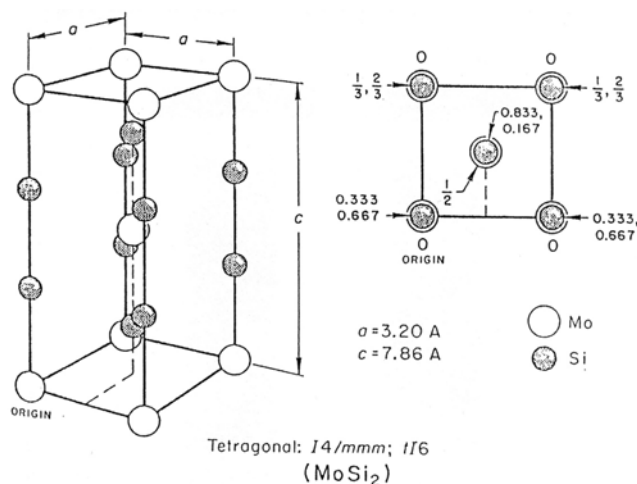
Table 1. Raw material used in the self-propagating high-temperature synthesis for producing molybdenum disilicide

Designation	Composition	Manufacture	Purity (%)	Mean particle size (μ m)	Remark
Mo	Mo	Hana Metal Co.	99.96	10	-
Si(1)	Si	Shinyo Co.	99.90	18	-
Si(2)	Si	Lucky Metal Co.	99.10	45-177	MG ^a

^aMG: Metallurgical grade.

Table 2. Thermodynamic properties of molybdenum and silicon compounds

Compound	Si/Mo	Heat of reaction Q (KJ/mole)	Melting temperature T _{mp} (°C)	Adiabatic reaction temperature T _{ad} (°C)	Crystal structure
Mo ₃ Si	0.3	97.534	2,025	930	Cubic
Mo ₅ Si ₃	0.6	272.927	2,180	1,327	Tetragonal
MoSi ₂	2.0	131.440	2,020	1,627	Tetragonal

**Fig. 3. Crystal structure of the tetragonal molybdenum disilicide.**

tant and product compositions was done by inductively coupled plasma and X-ray diffraction analysis. Surface area, pore volume, and pore size distribution were obtained by nitrogen adsorption and desorption techniques. Combustion temperature of powdered compacts was measured by using platinum-rhodium (13%) and platinum thermocouples and non-contact pyrometers. The propagation of combustion waves was recorded by a high-speed camera. Frame-by-frame analysis of the combustion wave propagation was done to characterize the mode of combustion and combustion rates.

RESULTS AND DISCUSSIONS

Molybdenum disilicide is the intermetallic between the molybdenum and the silicon elements. MoSi₂, Mo₅Si₃, and MoSi₃ compounds between the molybdenum and the silicon elements are formed depending on the atomic percent of silicon and the temperatures as shown in Fig. 2. The chemical reactions between the molybdenum and the silicon elements are described in Eqs. (1)–(3) to form the MoSi₂, Mo₅Si₃, and Mo₃Si, respectively. The physico-chemical properties of the products formed between the molybdenum and the silicon elements are summarized in Table 2. It is noted that the silicon may be melted during the combustion synthesis because the melting point of the silicon (1,414 °C) is less than the adiabatic reaction temperature forming the molybdenum disilicide (T_{ad}=1,627 °C). Molybdenum disilicide has a tetragonal crystal structure with lattice parameters of $a=3.20 \text{ \AA}$ and $c=7.86 \text{ \AA}$ as shown in Fig. 3.

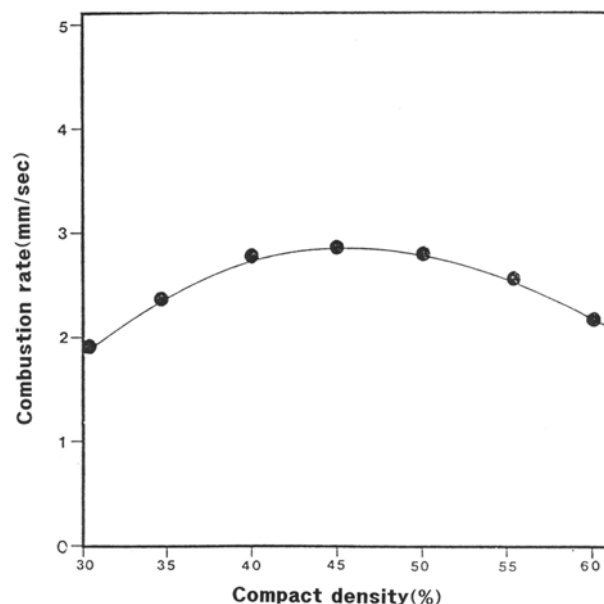
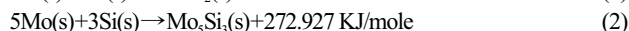
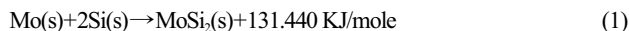
**Fig. 4. Effect of the compact density on the combustion rates for the Mo+2Si systems.**

Fig. 4 shows the dependence of combustion rates on the compact density for the Mo+2Si systems. Here the compact density is defined as the ratio of the bulk density of the compact to the theoretical density of MoSi₂, 6.31 g/cm³. The combustion rates increased with the increasing density of powdered compacts, reached a maximum combustion rate of 2.8 mm/sec at a compact density of 45%, and thereafter decreased with increasing density of powdered compacts. Combustion reactions did not occur at the density of powdered compacts less than 30% or higher than 60%. It was difficult to conduct the heat released from the high exothermic reactions at lower density of powdered compacts. The heat dissipation from the powdered compacts resulting from the higher rates of heat conduction is considerably increased at higher density of powdered compacts. Therefore, it was recommended that the density of powdered compacts should be maintained in the range of 30–60% for producing the molybdenum disilicide from the molybdenum and silicon powders. This result agreed well with the observation that stable combustions took place at a density of powdered compacts in the range of 40–65% [12]. It was observed that the combustion rates did not depend on the pressure of the inert argon gas at 1.0–10.0 bar [13].

The effect of the particle sizes of the silicon in powdered compacts on the combustion temperatures and rates is depicted in Fig. 5. The combustion temperatures and rates decreased with the increasing particle sizes of the silicon in the powdered compacts. It was difficult to ignite the powdered compacts with particle sizes of

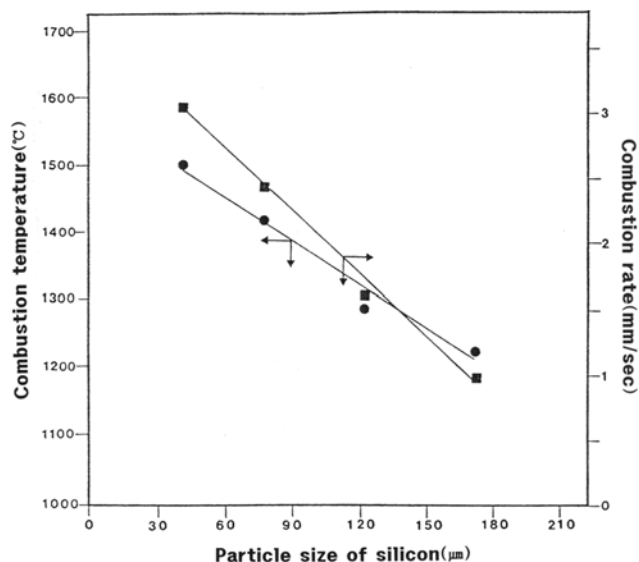


Fig. 5. Effect of the size of silicon particles on the combustion temperatures (●) and rates (■) for Mo+2Si systems.

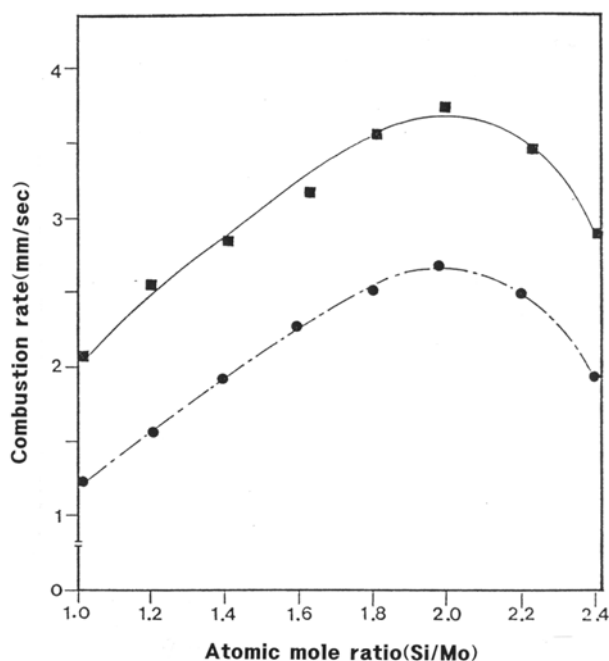


Fig. 6. Effect of the atomic ratio of silicon to molybdenum on combustion rates for molybdenum-silicon systems with (■) and without (●) preheating the compacts at 300 °C.

the silicon larger than 177 μm. Therefore, the particle sizes of the silicon less than 177 μm should be used for producing the molybdenum disilicide from the Mo+2Si reactants by combustion synthesis. The increased surface area for the smaller particles promoted the combustion reactions to result in the increased combustion temperatures and rates for the Mo+2Si systems. The maximum combustion temperature and rate at the particle size of the silicon powder at 45 μm turned out to be 1,500 °C and 3.0 mm/sec for the Mo+2Si systems, respectively. The combustion temperature, 1,500 °C, obtained at the particle size of the silicon at 45 μm may be very close

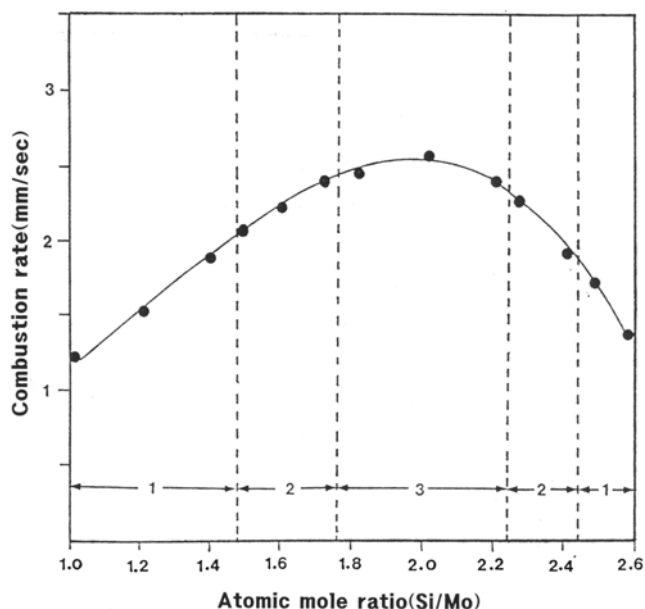


Fig. 7. Dependence of combustion rates on the atomic ratios of silicon to molybdenum for the molybdenum-silicon systems. Combustion is in the regime of spinning combustion (1), oscillatory combustion (2), and stable combustion (3), respectively.

to the adiabatic reaction temperature, 1, 627 °C for MoSi₂ [8].

Fig. 6 demonstrates the effect of the atomic ratio of silicon to molybdenum on the combustion rates with and without preheating the compacts at 300 °C, respectively. Combustion rates increased with the increasing atomic ratio of silicon to molybdenum in the powdered compacts, reached a maximum combustion rate of 2.6 mm/sec at an atomic ratio of silicon to molybdenum of 2.0. Preheating the powdered compacts at 300 °C promoted the combustion rate faster with a value of 1.0 mm/sec. With the values of the atomic ratio of silicon to molybdenum changing from 1.0 to 2.6, we observed combustion modes such as stable, oscillatory, and spinning combustions as shown in Fig. 7. Spinning combustions were observed with the values of the atomic ratio of silicon to molybdenum between 1.0 and 1.4. Oscillatory combustions were detected with the values of the atomic ratio of silicon to molybdenum between 1.5 and 1.7. Stable combustions were found with the values of the atomic ratio of silicon to molybdenum between 1.8 and 2.2. Oscillatory combustions were again observed with the values of the atomic ratio of silicon to molybdenum between 2.3 and 2.4. Finally, spinning combustions were also detected with the values of the atomic ratio of silicon to molybdenum between 2.5 and 2.6. SHS-produced molybdenum disilicide in the regime of stable combustions consisted of a uniform and single-phase MoSi₂, while SHS-synthesized molybdenum disilicide in the regime of unstable combustions was comprised of impurities such as Mo₅Si₃, Mo₃Si, unreacted Mo and Si except MoSi₂. Fig. 8 demonstrates the photographs of molybdenum disilicide produced by self-propagating high-temperature synthesis in the regime of stable, oscillatory, and spinning combustions comparing with that of compacted mixture of molybdenum and silicon powders. The bright layer of MoSi₂ and the dark layer of unreacted molybdenum and silicon were alternatively shown

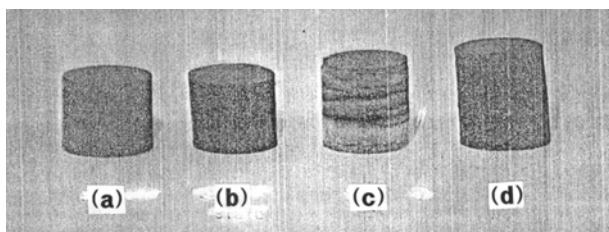


Fig. 8. Photographs of (a) the compact of molybdenum-silicon powders, molybdenum disilicide product under (b) stable combustion, (c) oscillatory combustion, and (d) spinning combustion, respectively.

as depicted in Fig. 8(c). Combustion fronts propagated only on the surface of the powdered compacts in the regime of spinning combustions to result in the unreacted molybdenum and silicon in the final products.

Shkadinskii's criterion α [11] is used to differentiate stable combustions from unstable ones as defined in Eq. (4). If $\alpha(\gamma_c, \beta_c) \geq 1$, the stable combustions take place. But If $\alpha(\gamma_c, \beta_c) < 1$, then the combustions proceed in the unstable regime. The decrease of combustion temperatures or the increase of the inert component in the powdered compacts may transfer the stable combustions to unstable ones.

$$\alpha(\gamma_c, \beta_c) = 9.1 \gamma_c - 2.5 \beta_c = 9.1 \times \frac{C_p RT_c^2}{QE} - 2.5 \frac{RT_c}{E} \quad (4)$$

where

C_p =specific heat capacity of product [J/mol·°C]

T_c =combustion temperature (\approx adiabatic reaction temperature) [°C]

Q =heat of reaction [J/mol]

E =activation energy [J/mol]

γ_c =dimensionless heat of reaction ($=C_p RT_c^2/QE$) [-]

β_c =dimensionless activation energy ($=RT_c/E$) [-]

As we changed the values of the atomic ratio of the silicon to molybdenum from 1.0 to 2.6, the values of α proposed by Shkadinskii et al. were calculated by Eq. (4), and the combustion modes observed in the combustion synthesis are recorded in Table 3. The value of criterion α turned out to be 0.74 for producing molybdenum disilicide from the constituent reactants by self-propagating high-temperature synthesis. Stable combustions may occur for the values of α greater than 0.74 ($\alpha > 0.74$) to give a uniform and single-

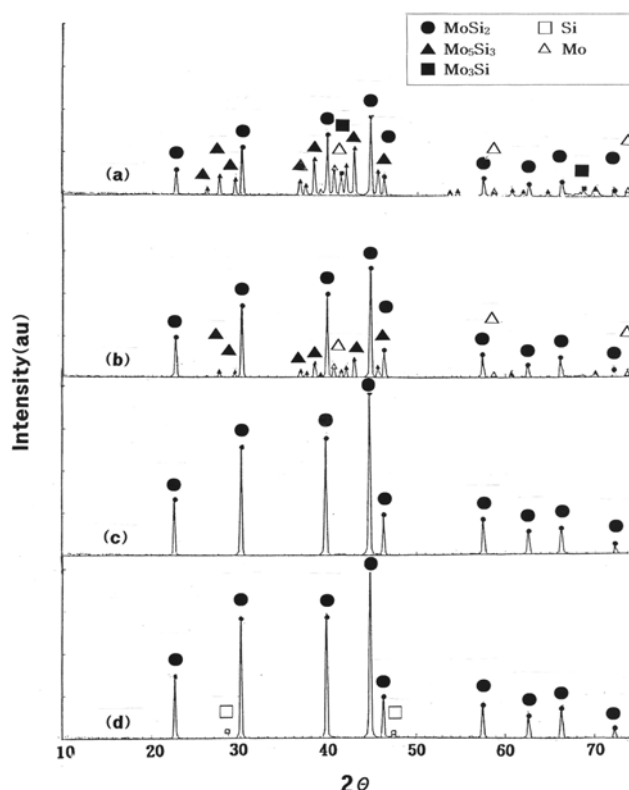


Fig. 9. XRD patterns for producing molybdenum disilicide depending on the atomic ratios of silicon to molybdenum at (a) Si/Mo=1.2, (b) Si/Mo=1.6, (c) Si/Mo=2.0, and (d) Si/Mo=2.4, respectively.

phased MoSi₂, while unstable combustions may take place for the values of α less than 0.74 ($\alpha < 0.74$) to result in a non-uniform and multiphase product. The difference of the values of α observed experimentally in this study ($\alpha=0.74$) from that proposed theoretically by Shkadinskii et al. ($\alpha=1$), might result from the fact that the combustion reactions did not take place adiabatically with uniform reactants and with the possible change of phases during the combustion reactions [15].

XRD patterns of the molybdenum disilicide produced from the molybdenum and silicon powders with the atomic ratios of the silicon to molybdenum at 1.2, 1.6, 2.0, and 2.4 are shown in Fig. 9.

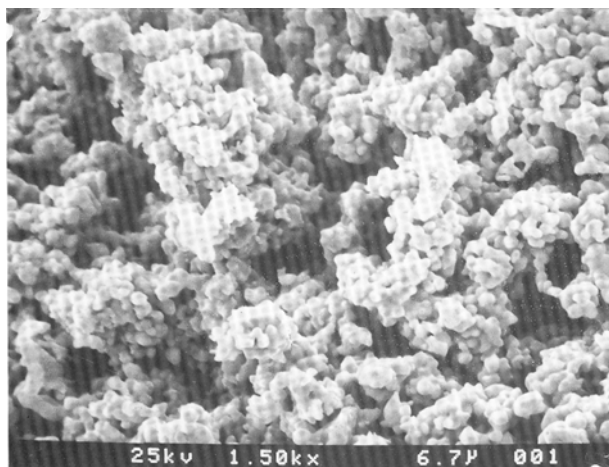
Table 3. Changes of α values with the atomic ratio of silicon to molybdenum for producing molybdenum disilicide by combustion synthesis

Si/Mo	Reaction temperature (°C)	Heat capacity ^a (J/mol·°C)	Heat of reaction ^a (KJ/mole)	α	Combustion mode
1.0	1,280	86.763	108.886	0.676	Spinning combustion
1.2	1,347	87.353	115.743	0.697	Spinning combustion
1.4	1,422	88.396	123.290	0.717	Spinning combustion
1.6	1,467	88.982	128.577	0.730	Oscillatory combustion
1.8	1,510	89.229	132.236	0.745	Stable combustion
2.0	1,570	90.154	139.285	0.765	Stable combustion
2.2	1,487	88.990	130.101	0.740	Stable combustion
2.4	1,387	87.793	119.573	0.710	Oscillatory combustion
2.6	1,337	87.199	114.403	0.693	Spinning combustion

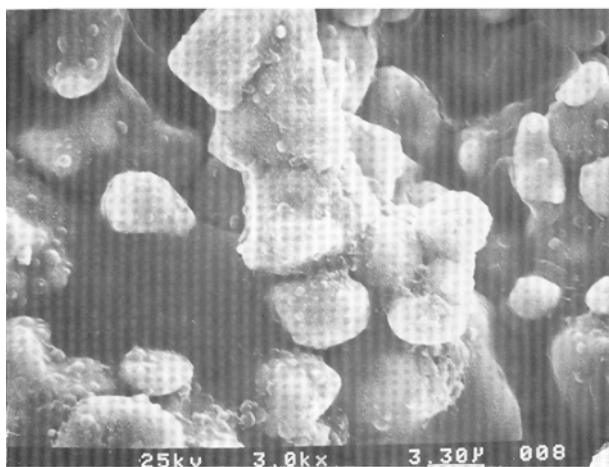
^aThese values were calculated by using the data in the handbook [14].

Table 4. Product composition depending on the atomic ratio of silicon to molybdenum reactants in the powdered compacts

Si/Mo	Product composition	Combustion mode
1.2	MoSi ₂ +Mo ₅ Si ₃ +Mo ₃ Si+Mo	Spinning combustion
1.6	MoSi ₂ +Mo ₅ Si ₃ +Mo	Oscillatory combustion
2.0	MoSi ₂	Stable combustion
2.4	MoSi ₂ +Si	Oscillatory combustion



(a)



(b)

Fig. 10. Scanning electron micrographs of the powdered compacts (a) before and (b) after the reaction for the Mo+2Si systems.

The composition of their products formed from their constituents by self-propagating high-temperature synthesis is summarized in Table 4. SHS-produced materials in the regime of stable combustions consisted of a uniform and single-phased MoSi₂, while SHS-produced materials in the regime of unstable combustions such as oscillatory, spinning, and surface combustions included the impurities of Mo₅Si₃, Mo₃Si, and unreacted Mo and Si to give lower degree of reaction and possibly poor electrical properties of heating element molybdenum disilicide. SEM pictures in Fig. 10 show the melting of the silicon during the self-propagating high-temperature synthe-

sis for the Mo+2Si systems. MoSi₂ produced from molybdenum having a surface area of 2.2 m²/g and silicon having a surface area of 4.0 m²/g had a lower surface area of 0.3 m²/g.

CONCLUSIONS

It is necessary to control the reactant composition, particle size of silicon, diameter and density of powdered compacts, and reaction atmosphere to produce a uniform and single-phased molybdenum disilicide for high-temperature heating elements by self-propagating high-temperature synthesis. The density of cylindrical compacts should be maintained in the range of 30-60% to result in the occurrence of combustion reactions. Stable combustions were observed for the values of the atomic ratio of silicon to molybdenum from 1.8 to 2.2 and SHS-produced materials consisted of a uniform and single-phased MoSi₂. In the meantime, unstable combustions such as oscillatory, spinning, and surface combustions were detected for values of the atomic ratio of silicon to molybdenum less than 1.8 or larger than 2.2. SHS-produced materials under unstable combustions included the impurities of Mo₅Si₃, Mo₃Si, and unreacted Mo and Si to give a lower degree of reaction and possibly poor electrical properties for the heating elements. Stable combustion may take place at the criterion α proposed by Shkadinskii et al. greater than 0.74 to give a uniform and single-phased MoSi₂.

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