A study of the combustion synthesis of MoSi$_2$ and MoSi$_2$–matrix composites

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The combustion synthesis of MoSi$_2$ from elemental powders was investigated. Higher completion of the reaction was achieved by the use of prior compaction of powders and higher heating rates. The reaction mechanism was studied by performing experiments at a heating rate of 20 K/min. It was established that reaction occurred via capillary motion accompanying the flow of molten silicon to the molybdenum powder particles. During the synthesis of MoSi$_2$/TiC composites, two ternary (Mo,Ti) Si$_2$ phases were observed, in contradiction to the thermodynamic predictions of the Mo–Si–Ti–C system. Combustion synthesis of (Mo, W) Si$_2$ yielded an inhomogeneous product where the composition of the solid solution varied throughout the sample. These observations were discussed in terms of the characteristics of the reaction process.

1. Introduction

As a result of a unique set of properties, MoSi$_2$ is emerging as a promising structural material for high temperature applications. The combination of attractive properties includes a high modulus of elasticity, a high melting point (2303 K) and an excellent oxidation resistance at high temperatures [1]. The versatility of the material is demonstrated by its use for heating elements in furnaces operating in air at temperatures as high as 1973 K. MoSi$_2$ is brittle at room temperature due to a low dislocation mobility which is overcome with the help of thermal activation at higher temperatures. The material therefore undergoes a brittle-to-ductile transition at a temperature of about 1173 K [2,3] and so its failure behaviour becomes more predictable. In this respect MoSi$_2$ is competitive with other silicon-based materials like SiC and Si$_3$N$_4$ which remain brittle from room to high temperatures. However, its room temperature toughness as well as its high temperature strength need to be improved if MoSi$_2$ is to be used successfully in structural engineering applications. One way of extending the creep resistance of the material is via the incorporation of a second phase like Mo$_5$Si$_3$ [4, 5] and SiC, both as particulates [6] and as whiskers [7, 8], or by the addition of WSi$_2$ [6] to form a (Mo, W) Si$_2$ solid solution.

MoSi$_2$ can be synthesized by various processes which may involve arc-melting and casting, sintering and hot-pressing [9, 10]. The major disadvantage of such processes is that they require high temperatures and therefore high energy costs. More advanced techniques like mechanical alloying have also been used [11, 12]. However, very careful control of the processing environment and the impurity content must be exercised in order to avoid the formation of amorphous SiO$_2$ which has a detrimental effect on the creep

strength of the material [11]. In recent years there has been an increasing interest in self-propagating high temperature synthesis (SHS) as an alternative production route for metallic and ceramic materials as well as composites [13]. The process is based on highly exothermic reactions where the reactants spontaneously transform to products following initiation of the reaction. The reaction can occur in the form of an explosion or wave propagation and because of its nature it is invariably complete within seconds rather than hours which is common for conventional processing. The technique is also capable of producing composite materials with a uniform dispersion of fine reinforcement particles in a single-stage process. In addition it can be adapted to synthesize near-net shape components by the simultaneous application of pressure. MoSi$_2$ can be prepared by SHS by interaction between elemental molybdenum and silicon powders making use of the high enthalpy of formation of the disilicide ($\Delta H^o_{f,298\,K} = -131.8$ kJ per mol MoSi$_2$) [14]. The formation of MoSi$_2$ by SHS has previously been studied in some detail by Deevi [15] who supplied a pulse of current to an ignition coil which was touching the reactants, in order to generate the reaction. The objective of the present work was to further examine the reaction characteristics for the formation of MoSi$_2$ as well as MoSi$_2$–SiC and MoSi$_2$–TiC composites using preheating as a means of ignition. In some experiments tungsten powder was added in order to investigate the production of a (Mo, W) Si$_2$ solid solution.

2. Experimental procedure

Elemental powders of molybdenum, silicon, titanium, tungsten and carbon in the form of graphite were used

TABLE I The raw materials used during the study

Element	Average particle size	Purity
Mo	4–8 µm	99.9%
Mo	< 80 µm	99.9%
Si	5 µm	97.5%
Graphite	5 µm	99.5%
Ti	< 45 µm	99.9%
W	5 µm	99.9%

as the raw materials during the study (for details, see Table I). Experiments were conducted using molybdenum powders of two different particle sizes in order to compare the reaction characteristics. The required amounts of the reactant powders were weighed and mixed thoroughly. The reacting mixtures weighed a total of 20 g and were heated to ignition in a graphite crucible, using an induction furnace. While in most experiments the heating rate was controlled to 20 K min^{-1}, some runs were performed at a heating rate of about 200 K min^{-1}. All experiments took place in the presence of flowing argon. The induction heating was stopped upon ignition of the sample and the reaction was allowed to self-propagate. Some experiments were also carried out in a differential calorimeter (Model STA–780) at a heating rate of 20 K min^{-1} in order to obtain accurate values of the ignition temperature. Phase identification was carried out using X-ray diffraction (XRD) with copper K_α radiation. Microscopic characterization was performed using optical as well as scanning electron microscopy (SEM) on a Jeol JSM 8600, microscope.

3. Results and discussion

3.1 Effect of particle size, heating rate and precompaction

The self-propagating reaction between Mo and Si was observed to take place following sufficient preheating. Various runs were carried out in a differential calorimeter to examine the effect of the molybdenum particle size on the ignition temperature. While using a constant heating rate of 20 K min^{-1}, the reaction between silicon and molybdenum of particle size less than 80 µm ignited at 1383 K, whereas for a Mo particle size between 4–8 µm a temperature of 1361 K was recorded. The decrease in the ignition temperature with decreasing molybdenum particle size was in fact expected since the finer powder provided an increase in the surface area of one of the reactants. In both cases the reaction was incomplete with small amounts of unreacted molybdenum and silicon present, in addition to tetragonal $MoSi_2$, Mo_3Si and Mo_5Si_3. The amount of unreacted Mo and Si was much less in the sample with the finer Mo particle size. The products as well as the extent of reaction were observed to vary not only with particle size and the heating rate but also with the condition of the reactant powders i.e., whether they were in a compacted state or not. A full reaction was observed to take place only when the compacted reactants were ignited by preheating at a rate of 200 K min^{-1}. It was therefore concluded that

incomplete reaction occurred as a result of the starting materials being in the form of loose rather than compacted powder and also due to a slow heating rate.

Precompaction was rather crucial in obtaining a complete reaction because it gave a relatively better contact between the reactants and also provided a more efficient means of heat transfer as the wave propagated through the sample. This observation was in line with the work of Deevi [15] who suggested that green compacts of at least 59% theoretical density were necessary to produce single phase $MoSi_2$ by the combustion reaction of the elemental powders. From the point of view of producing $MoSi_2$, a low heating rate would be undesirable because it increases the time available for solid–solid diffusion reactions between molybdenum and silicon to take place at low temperatures and thus, encourages the nucleation of subdisilicide phases. The development of a subdisilicide layer around the surface of molybdenum makes the access of silicon to the metal more difficult once ignition of the reaction takes place.

3.2. Examination of the mechanism of reaction

In order to gain better control of the SHS process it is necessary to identify the basic steps involved. The present work has shown that by lowering the heating rate it is possible to alter the extent of reaction so that some mechanistic information can be obtained. This observation provided the opportunity to investigate the reaction mechanism by examining samples during the intermediate stages of the reaction. Upon ignition, the reaction between the two elements took place via the wave propagation mode of SHS. The wave required approximately 6–8 sec to propagate through the entire sample. Examination of the product showed the development of wave patterns on the sample surface as presented in Fig. 1. The point where the waves radiate from was clearly the point of origin of the reaction. The final product was not in the form of loose powder, but a bonded mass. This observation provided evidence that some melting or sintering of the samples had taken place.

Examination of samples by SEM showed large areas of macrosegregation. On the outside portion of the samples a faceted grain structure of $MoSi_2$ was observed within a matrix of unreacted silicon as shown in Fig. 2. No unreacted Mo was observed within the outer part of the product samples. Using a thermodynamic analysis previously presented by Subrahmanyam et al [16], the amount of molten phase resulting from an ignition temperature of 1383 K was estimated to be around 50%. The faceted $MoSi_2$ grains in Fig. 2 developed from molten $MoSi_2$. Within the central regions of the samples, Mo_5Si_3 was detected in addition to $MoSi_2$ and some Mo_3Si together with unreacted molybdenum. Evidently one of the reasons the reaction did not go to completion was due to the separation of molten Si from the solid Mo. These observations were further investigated by carrying out a combustion reaction using Mo and Si as starting materials in an atomic ratio of Mo:Si of 5:3.
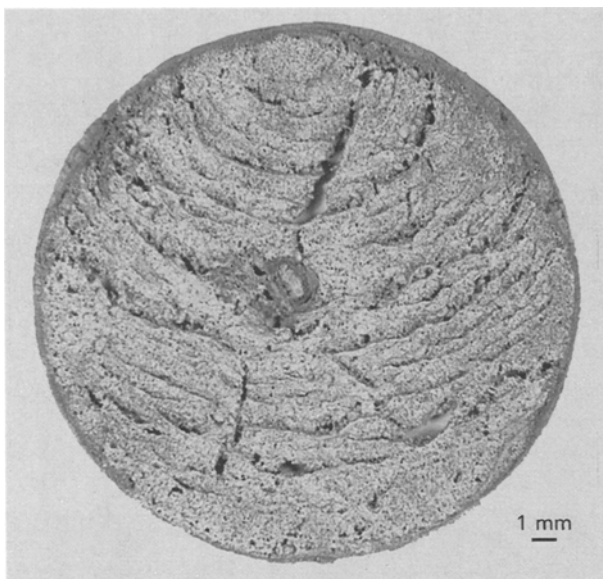
Figure 1 Optical micrograph of a reacted sample showing the radiation of waves from the ignition point.
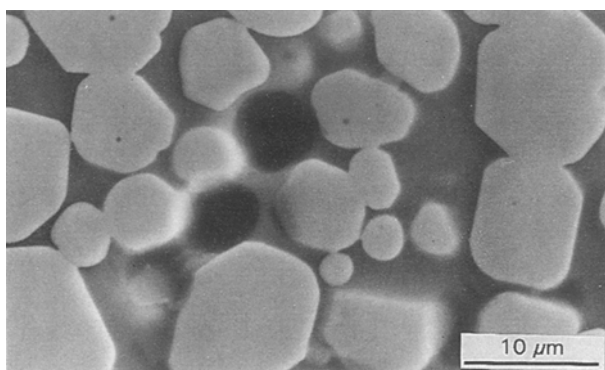

Figure 2 SEM micrograph showing faceted grains of $MoSi_2$ in a matrix of unreacted silicon.

Figure 3 Backscattered imaging SEM micrograph showing cores of unreacted Mo surrounded by Mo_3Si(dark grey) in a matrix of Mo_5Si_3.

Figure 4 SEM photograph of $Mo_5Si_3/MoSi_2$ eutectic; Mo_5Si_3 (white), $MoSi_2$(dark grey).

The object of reducing the amount of elemental silicon in the starting materials was to encourage the formation of the sub-disilicide phases. Indeed, XRD data from this experiment indicated the presence of a larger amount of Mo_3Si together with Mo_5Si_3, $MoSi_2$ as well as unreacted Mo and Si. Macrosegregation of the products was again in evidence as before. Characterization using SEM showed in some areas the development of molybdenum cores which were surrounded by Mo_3Si in a continuous matrix of Mo_5Si_3 as presented in Fig. 3. It was noticeable that the Mo cores were always detached from the surrounding Mo_3Si. A large degree of porosity was evident in these regions. The pores were well-distributed and rather fine and were almost invariably surrounded by the Mo_3Si phase. The pores in the final structure were therefore concluded to occupy the positions where molybdenum was originally present. Since a relatively low heating rate was used to heat the elemental powders, in some regions solid Mo–solid Si interactions took place prior to ignition. The diffusion rate of silicon into molybdenum is faster than that of molybdenum into silicon. Initial reaction was therefore dominated by
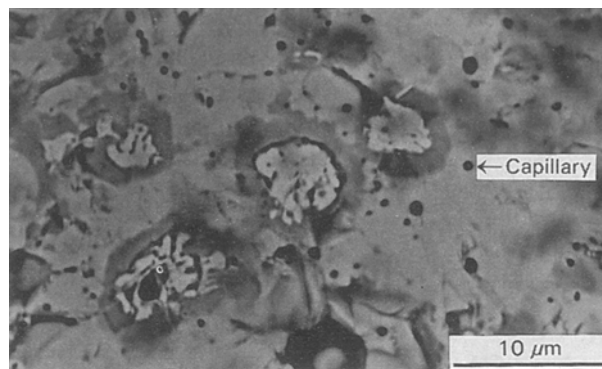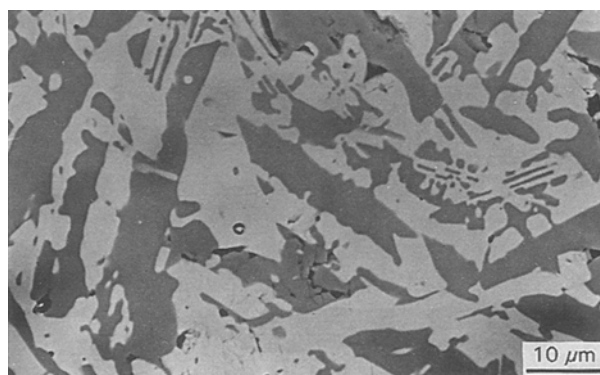
the diffusion of Si into Mo. The first product species was Mo_3Si at the Mo surface. Following ignition of the reaction and the release of exothermic heat, silicon melted at 1783 K and this increased its mobility and high diffusion rates were established as Mo_5Si_3 and $MoSi_2$ started to form. SEM examination indicated features of partial melting of the Mo_3Si and Mo_5Si_3 phases. Energy dispersive spectroscopy (EDX) analysis showed that in some cases a small amount of unreacted Si was present also within the molybdenum cores. The melting of silicon enabled it to diffuse to the solid molybdenum particles. Even if Mo was surrounded by solid silicide phases, it would still be accessible by molten Si via capillary motion. This view is supported by the presence of capillaries extending from the matrix to the Mo/Si cores and by the fact that the central cores were invariably detached from the surrounding product phases. Reaction then took place at the periphery of the molybdenum particles to initially yield Mo_3Si which developed as a detached layer surrounding the Mo/Si cores. The Mo_3Si layer subsequently reacted with the surrounding molten silicon (rather than the silicon in the Mo/Si cores) to produce Mo_5Si_3 and then $MoSi_2$. In other areas of the sample where melting of the Mo_5Si_3 and $MoSi_2$ phases occurred, a eutectic microstructure of the two was observed as presented in Fig. 4.

Macrosegregation was one of the most striking features of the microstructures examined. The creation of

colonies of $MoSi_2$ in a matrix of unreacted Si in the outer regions of the samples and the detection of Mo_3Si/Mo_5Si_3 colonies and $MoSi_2/Mo_5Si_3$ eutectic microstructures was the result of segregation of molten Si from Mo. The nature of the reaction was such that it became quenched well before completion. According to Munir [17] for a self-propagating reaction to occur, the ratio of the enthalpy change for the reaction to the specific heat capacity of the products, $\Delta H^\circ_{298 K}/C_{p\ 298 K}$ must exceed 2000. In the case of $MoSi_2$ this value is 2054, only marginally above the expected figure for self-propagation. The use of loose powders resulted in heat loss from the wave front so that energy starvation prevented the reaction from going to completion and thus resulted in the development of macrosegregated features.

3.3 Combustion synthesis of MoSi₂–matrix composites

Macrosegregation was also observed as a result of reactions to form $MoSi_2$–SiC composites. $MoSi_2$ grains surrounded by unreacted silicon were generally observed around the periphery of the product samples as illustrated already in Fig. 2. The reaction did not go to completion as a result of the use of loose powders and a low heating rate. Fig. 5 shows $MoSi_2$ grains with a $MoSi_2/Mo_5Si_3$ eutectic microstructure at the grain boundaries and a fine distribution of SiC particles. It is interesting to note that the SiC was found within the eutectic structure indicating that it developed after the formation of the $MoSi_2$ matrix.

XRD data from the reaction of Mo, Si, Ti and graphite mixtures at a heating rate of $20\ K\ min^{-1}$ indicated the production of Mo_5Si_3, TiC and a tetragonal phase based on $MoSi_2$. EDX analysis revealed that up to 2 wt % Ti had dissolved in the matrix which was in fact tetragonal $(Mo, Ti)Si_2$ which is isomorphous with $MoSi_2$. In addition to this, fine precipitates of another Mo–Si–Ti phase were observed by SEM as shown in Fig. 6. The amount of this ternary phase was too small to be detected by the available diffractometer. However, on the basis of EDX analysis, it contained about 7 wt % Ti and was thought to be the hexagonal C40 $(Mo, Ti)Si_2$ structure. The observation of the two $(Mo, Ti)Si_2$ phases was rather surprising because a thermodynamic analysis of the Mo–Ti–Si–C system per gram atom of Mo or Ti (Fig. 7) based on data provided by Thermocalc [18] indicated that TiC was the most stable phase in the system and would be expected to form under equilibrium conditions. No thermodynamic data were available for the $(Mo, Ti)Si_2$ phases so they were not considered in the thermodynamic assessment of the system. However, it is reasonable to assume that the value of the free energy of formation of the $(Mo, Ti)Si_2$ phases will be fairly close to that of $MoSi_2$ and $TiSi_2$ both of which have similar free energy values. Thus, it would be unlikely for the ternary phases to form under equilibrium conditions. Based on these observations it was concluded that the system never reached equilibrium and the ternary silicides formed instead which are thermodynamically metastable with respect
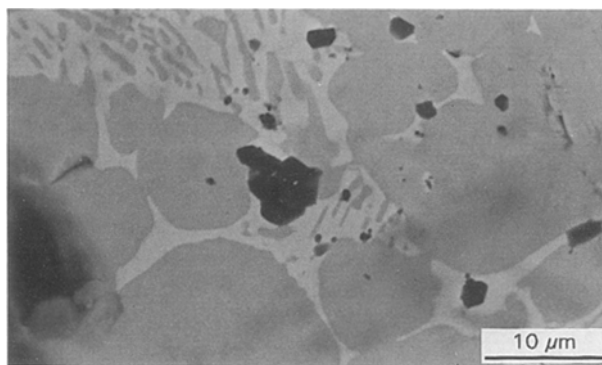

Figure 5 Backscattered image micrograph showing $MoSi_2$(dark grey), $MoSi_2/Mo_5Si_3$ eutectic and SiC particles(black).

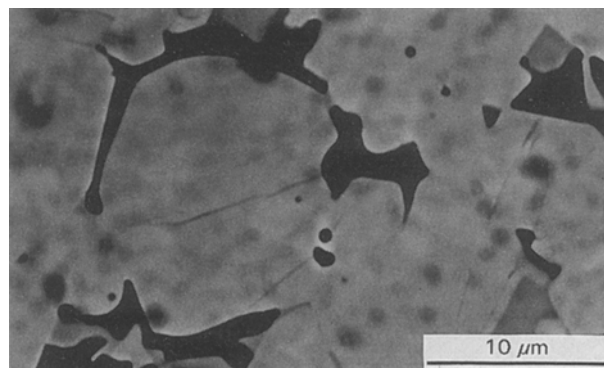*Figure 6* Backscattered image showing Mo_5Si_3(white), $(Mo, Ti)Si_2$ containing about 2 wt % Ti(black) and $(Mo, Ti)Si_2$ containing 7 wt % Ti(grey).
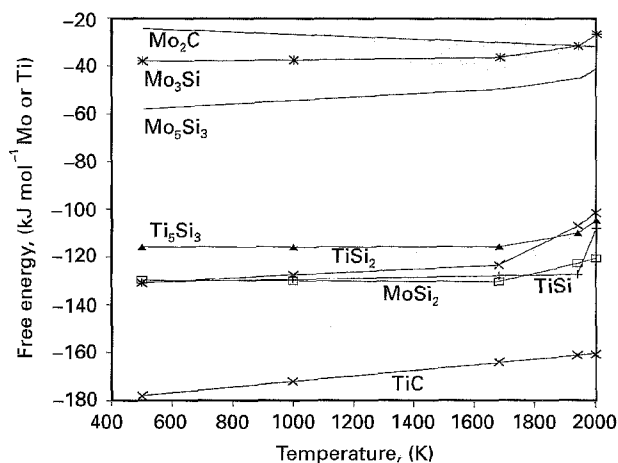

Figure 7 Plot of free energy of formation of the carbides and silicides of Mo and Ti per mole of the metal.

to TiC. On ignition of the reaction, both Si and Ti melted (melting points of 1685 K and 1943 K respectively), while at the same time TiC and the molybdenum silicide phases were being formed. The lattice parameter of the carbide observed during this work was about 0.43315 nm which according to data compiled by Storms [19] corresponded to a carbide composition of $TiC_{0.85}$. At the adiabatic temperature some of the reacting Ti probably formed a liquid Mo–Si–Ti solution which has a peritectic temperature of around 2110 K [20]. The presence of the molten

ternary silicide at the adiabatic temperature together with the relatively fast cooling rate that followed changed the mechanism of the reaction. Consequently, the two $(Mo, Ti)Si_2$ phases were precipitated in the final product. The formation of $(Mo, Ti)Si_2$ by combustion of $(Mo + Si + Ti + C)$ mixtures was also reported by Subrahmanyam et al. [16]. However, it was quite surprising to note that these authors also observed the presence of the ternary silicide when 40 wt % TiC powder was used to moderate the combustion reaction between Mo and Si. This observation would be possible only if the authors used TiC which was highly deficient in carbon because the thermodynamic stability of the carbide is dependent on its composition [21]. Unfortunately the TiC composition was not stated by the authors [15].

Some combustion experiments were carried out by making additions of up to 20 % W in order to synthesize a $(Mo, W)Si_2$ solid solution. $MoSi_2$ and WSi_2 form a complete solid solution with each other [22]. XRD analysis confirmed the formation of both $(Mo, W)Si_2$ and $(Mo, W)_5Si_3$ solid solutions. Close examination of the microstructure revealed that the $(Mo, W)Si_2$ solid solution was inhomogeneous with a large variation in its composition. This is illustrated in the micrograph in Fig. 8 which shows a backscattered image of the product microstructure. The variation in the colour of grains signifies a variation in the composition of the disilicide solid solution, the darker colours indicating an increased tungsten concentration. Whilst the $(Mo, W)_5Si_3$ phase which appears white in the micrograph had more or less a homogeneous composition containing about 8 wt % W, the composition of $(Mo, W)Si_2$ varied throughout the sample. Once again the heat loss from the sample played an important role in preventing the completion of the reaction. In addition to this, the enthalpy of formation, $\Delta H^o_{f, 298 K}$, of $WSi_2(-92.9 kJ mol^{-1})$ is less negative than that of $MoSi_2$ [13] and this resulted in a drop in the combustion temperature. The resulting lower combustion temperature led to a decrease in the rate of diffusion and was therefore a significant factor in the development of an inhomogeneous product.
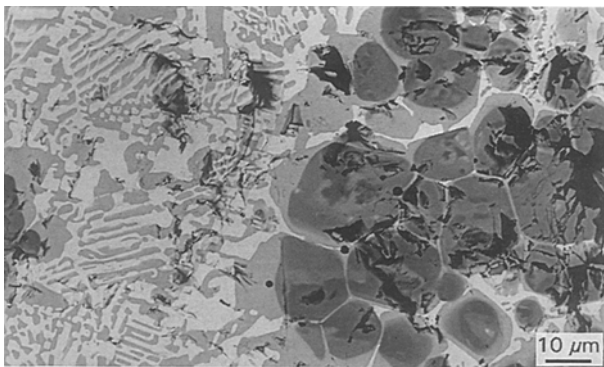

Figure 8 Backscattered image showing a variation in the composition of the $(Mo, W)Si_2$ solid solution (dark grey areas are richer in W).

4. Conclusions
The present work has shown that a higher conversion to $MoSi_2$ was achieved by SHS by precompacting the reactant powders and increasing the heating rate. Precompaction tended to reduce the rate of heat loss from the sample and led to a higher yield. A lower heating rate encouraged the nucleation of larger amounts of the sub-disilicide phases and this prevented the reaction from going to completion. For the same reason the ignition temperature increased by lowering the rate of heating of the reactants.

The resulting microstructures were fairly inhomogeneous with a product variation resulting throughout the samples. Examination of the reaction at a heating rate of 20 K min^{-1} indicated the diffusion of molten Si to Mo particles by capillary motion. During reactions to form $MoSi_2–TiC$ composites, it was surprising to observe the presence of two ternary phases based on $(Mo, Ti)Si_2$. These phases which are metastable with respect to TiC formed from the molten Mo–Si–Ti solution and were the result of the relatively fast cooling rate after attainment of the combustion temperature. Finally, the inability to drive the reaction to full conversion led to a highly inhomogeneous $(Mo, W)Si_2$ solid solution throughout the product microstructure.

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