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Synthesis of molybdenum silicides by the self-propagating combustion method

S. ZHANG*, Z. A. MUNIR
Division of Materials Science and Engineering, College of Engineering, University of California, Davis, CA 95616, USA

The synthesis of the silicides of molybdenum (Mo_3Si, Mo_5Si_3, and $MoSi_2$) by the self-propagating combustion method is investigated. Only the reactants corresponding to the last phase can be reacted in a self-sustaining mode without preheating. The product of such a reaction is single-phase $MoSi_2$. Although reactant mixtures corresponding to the other two silicides can react in a self-sustaining mode with prior heating, the products of combustion were multi-phase. The dependence of the combustion temperature and velocity on the stoichiometry of the silicide was determined. The activation energy for the combustion synthesis of $MoSi_2$ determined in this investigation, 139.4 kJ mol^{-1}, is considerably lower than activation energies reported for the diffusion of silicon in molybdenum or in $MoSi_2$.

1. Introduction

Molybdenum disilicide and similar materials are of current interest because of their high stability in oxidizing and corrosive environments [1, 2]. They are useful in such applications as heating elements, thermoelectrodes, protective thermocouple sheaths, gas turbine components, hot-pressing and drawing dies [3–5], and as catalysts for the dehydrogenation of alcohols [6].

Molybdenum disilicide is usually produced by reacting the powdered elements at relatively low temperatures (typically 1200 °C for ~ 2 h). The product of such reaction is in the form of hard sintered compacts which are broken up and milled to produce powders of $MoSi_2$ for subsequent processing.

The utilization of the self-propagating high-temperature synthesis (SHS) for the preparation of a variety of high-temperature materials has been demonstrated in numerous investigations. A detailed description of this method and its general advantages are provided in two recent review articles [7, 8]. The synthesis of $MoSi_2$ by the SHS method has been shown to provide a product with reduced O_2 contamination [9] and which is more sinterable than conventionally produced materials [10]. In this paper we report the results of an investigation on the effect of stoichiometry, preheat temperature, and initial density of samples in the Mo–Si system on their synthesis by the SHS method.

As can be seen from the phase diagram for the Mo–Si systems, Fig. 1 [11], equilibria between silicon and molybdenum results in the formation of three compounds with well-defined compositions corresponding closely to the formulae Mo_3Si, Mo_5Si_3, and $MoSi_2$. The last two phases are congruently melting compounds with melting points of 2195 and 2045 °C, respectively, while the first undergoes melting through a peritectic decomposition at 2117 °C. In the present study we investigated the combustion behaviour of reactant mixtures with compositions ranging from about 9–48 wt % Si, i.e. representing Mo/Si atomic ratios ranging from 3.0–0.3.

The adiabatic combustion temperatures for the three molybdenum silicides are listed in Table I. These values were calculated from published enthalpies of formation and heat capacities for the silicides [12]. Also listed in Table I are the ratios $\Delta H^\circ_{f298}/C_{p298}$ where ΔH°_{f298} is the heat of formation of the silicide at 298 K and C_{p298} is its heat capacity at that temperature. On the basis of experimental observations, it has been suggested that systems with $T_{ad} \lesssim 1800$ K will not react in a self-propagating manner [13, 14]. More recently, it was shown that the ratio $\Delta H^\circ_{f298}/C_{p298}$

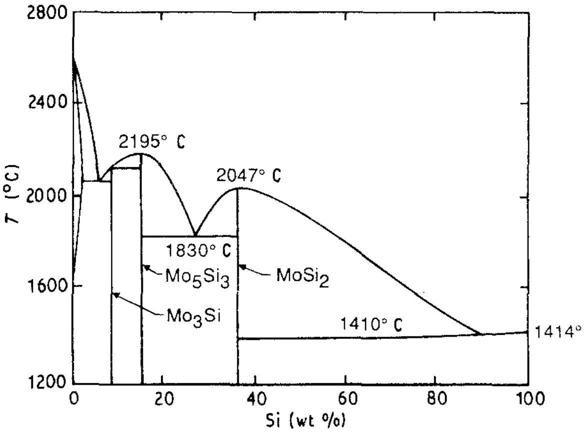

Figure 1 The Mo–Si phase diagram.

**Permanent address*: Research Institute for Light Materials Source, Nanjing, People's Republic of China.

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TABLE I Adiabatic combustion temperatures and thermodynamic data for molybdenum silicides

Compound	T_{ad} (K)	$\Delta H^{\circ}_{f298}/C_{p298}$ (10^{-3} K)
Mo_3Si	1423	1.27
Mo_5Si_3	1725	1.72
$MoSi_2$	1913	2.05

for the product of combustion can be used, likewise, as a predictive parameter for the occurrence of a self-sustaining reaction [7]. A ratio of 2.0×10^3 is suggested as the delineating value, below which reactions are not self-sustaining. From both of these empirical criteria, it can be assumed that a self-sustaining combustion process can only be established in the case of $MoSi_2$ if the reactants are not preheated before ignition.

2. Materials and methods

The materials used in this study were 99.9% pure Mo powder with a particle size range 3–7 μm and 99.5% pure Si powder with a sieve classification of − 325 (≤ 44 μm) and an average size of 10 μm. The powders were mixed in the desired stoichiometry and pressed into cylindrical specimens with typical dimensions of 19.1 mm diameter and 22.9 mm length. The cylindrical pellets were combusted inside a glass reaction chamber under 1 atm pressure of flowing Ar. The purity of the Ar gas was reported as 99.98%. To increase the initial reaction temperature, T_0, samples were heated by radiation from a W wire surrounding each specimen. To ignite the specimen, radiative heat was directed to its upper face from a heated W coil placed 2–3 mm above it. The combustion temperature, T_c, associated with the passage of the combustion wave was determined from the output of a W–5%Re/W–26%Re thermocouple placed inside a small hole drilled in the side of each specimen. The velocity of the combustion wave was determined by timing the interval of propagation between two fixed locations on the sample. The composition of the products of combustion was determined through X-ray diffraction analysis. To investigate the influence of the relative density of reactants on the combustion synthesis of $MoSi_2$, the powder mixtures were pressed (at different applied pressure) to give densities ranging from about 43%–63% theoretical.

3. Results and discussion

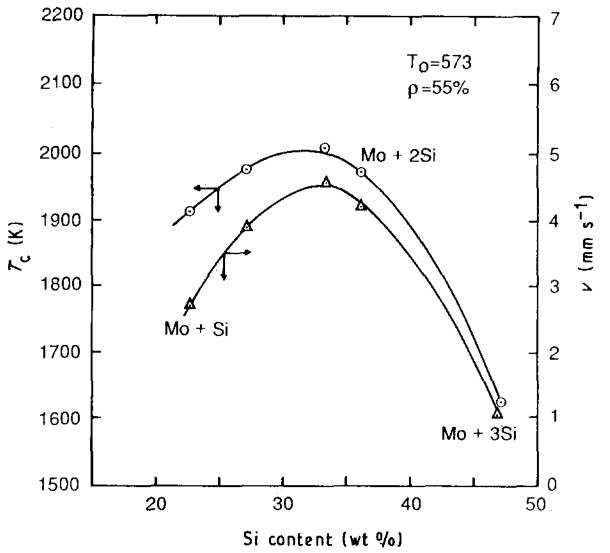

Figure 2 The effect of the Si content on the combustion temperature and wave velocity. $T_0 = 573$ K, $\rho = 55$ %.

Mixtures of Mo and Si powders in the proportion corresponding to Mo_3Si (8.9 wt % Si) could not be ignited even after preheating to 500 °C. However, mixtures corresponding to the compound Mo_5Si_3 (14.9 wt % Si) could be ignited if they were preheated to this temperature. In such a case, a self-propagating wave was established and it propagated across the entire sample. However, when the preheating temperature was lowered (to 400 or 300 °C), the pellets of mixtures of 5Mo + 3Si could be ignited, but the combustion front was not self-sustaining. Under these conditions the wave propagated halfway down the sample and then became extinguished. As the content of Si in the reactants increased, the combustion process tended to intensify as indicated by an increase in the temperature and velocity of combustion as seen in Fig. 2. The values of these parameters, however, reached a maximum near a composition of about 27 wt % Si (near the eutectic composition). In the compositional range of 27–36.8 wt % Si, the combustion synthesis can be self-sustaining without preheating, i.e. with $T_0 = 298$ K. When the Si content was increased beyond that corresponding to $MoSi_2$, the combustion process became less intense, as seen in Fig. 2. The results shown in this figure were obtained with samples preheated to 300 °C.

X-ray analyses of phases produced from samples containing different amounts of Si are given in Table II. As can be seen from these results, in all but the Mo + 2Si mixture, the product of combustion is multiphase. As the composition of the reactants decreased from ~ 37 wt % Si (corresponding to $MoSi_2$), the product contained progressively higher amounts of Mo_5Si_3 and Mo with the relative abundance of these two phases also shifting. For example, at ~ 15 wt % Si the product contained Mo as the principal phase. On the other side of the Mo + 2Si composition (i.e. at Si > 37 wt %), the product contained unreacted Si.

As was discussed earlier, preheating was necessary to establish a self-propagating wave in certain compositions in the Mo–Si systems. In the case of

TABLE II Composition of products of SHS reactions in the Mo–Si system

Si (wt %)	Atomic mixture	Phases in product[a]
15	5Mo + 3Si	Mo, Mo_5Si_3, $MoSi_2$
22	Mo + Si	$MoSi_2$, Mo_5Si_3, Mo
27.1	—	$MoSi_2$, Mo_5Si_3, Mo (minor)
37.5	Mo + 2Si	$MoSi_2$
48	Mo + 3Si	$MoSi_2$, Si

[a] Phases are reported in order of decreasing relative abundance.

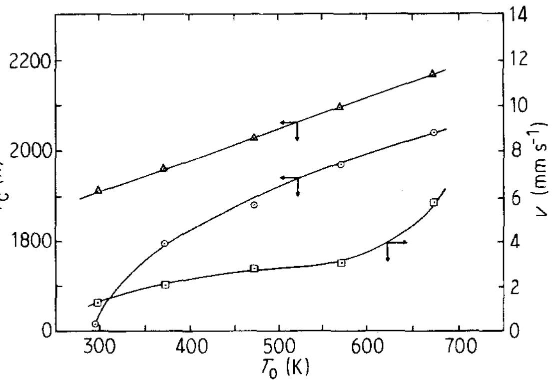

Figure 3 The effect of the initial temperature on the velocity and calculated and experimental temperatures of combustion for Mo + 2Si. T_c: (△) calculated (T_{ad}), (⊙) measured. V: (⊡) measured.

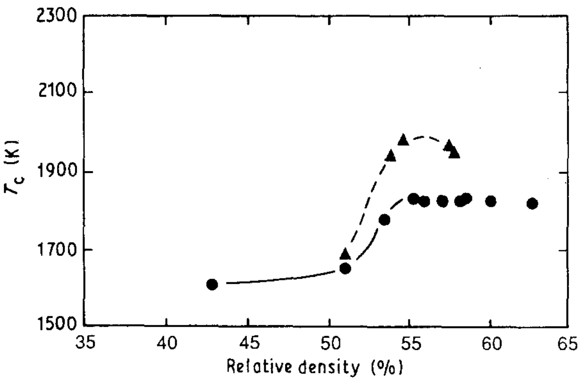

Figure 5 The effect of relative density on the combustion temperature for $MoSi_2$. T_0 (K): (●) 298, (▲) 573.

Mo + 2Si mixtures, preheating was not necessary but its influence on the temperature and velocity of combustion was investigated. To establish a uniform temperature prior to igniting the sample, preheating was carried out for 15–20 min at the selected temperature. The effects of the preheating temperature, T_0, on the combustion temperature, T_c, and wave velocity, v, are shown in Fig. 3. Fig. 3 also includes the effect of the preheat temperature on the calculated adiabatic temperature, T_{ad}. The difference between the experimental and calculated values is a consequence of the lack of adiabatic conditions due to heat loss to the environment.

The effect of the relative density of the reactants on the wave velocity and temperature of combustion in the synthesis of $MoSi_2$ was also investigated. Fig. 4 shows the results of the effect of density on the wave velocity for samples ignited without preheating and for samples ignited after preheating at 300 °C for 15 min. In both cases, the velocity increased with increasing density. However, in the case of the unheated samples an anomaly was observed in the density range between about 55% and 60%. In this range the velocity decreased and then increased, as shown in Fig. 4. It was determined that this behaviour was related to the mixing of the initial powders. When pressed compacts were broken up and repressed and ignited, the anomalous behaviour was not observed as shown in Fig. 4. Similar anomalous behaviour of the temperature of combustion was also observed over approximately the same density range (55%–60%), and again it was found that the repressing of the reactant samples eliminated this behaviour. The results shown in Fig. 5 for the unheated samples are those in which the samples were repressed. As expected, the preheating of the samples resulted in an increase in the combustion temperature [15] and a corresponding increase in the velocity of the combustion wave [16]. The effect of the preheating temperature on the observed and calculated combustion temperature (T_c and T_{ad}, respectively) for samples with a constant relative density (~ 53%) is shown in Table III.

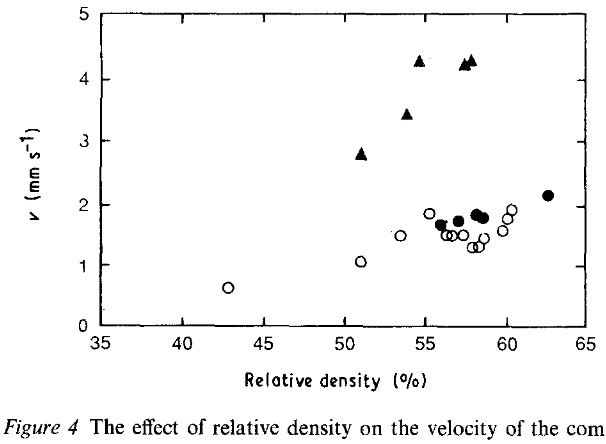

Figure 4 The effect of relative density on the velocity of the combustion wave for $MoSi_2$. Recompacted samples. T_0 (K): (○) 298, (▲) 573, (●) 298.

Determinations of the mechanism of SHS reactions have been made primarily by two analytical approaches. In the first approach, the temperature dependence of the velocity of wave propagation is used to calculate the activation energy, E, of the process [16], and in the second approach the temperature profiles of the wave are used to obtain the kinetic function, E [17].The relationship between the velocity of wave propagation, v, and the combustion temperature, T_c, has the following form [18, 19]

$$v^2 = f(n)\frac{C_p k}{q}\frac{RT_c^2}{E}K_0 \exp(-E/RT) \qquad (1)$$

where $f(n)$ is a function of the kinetic order, n, of the reaction, C_p and k are, respectively, the heat capacity and thermal conductivity of the product, q is heat of the reaction, T_c is the combustion temperature, R is the gas constant, and K_0 is a constant. Thus, from a plot of ln (v/T_c) versus $1/T_c$, the activation energy can be calculated. Such a plot is shown in Fig. 6 for the

TABLE III Effect of preheating on the combustion temperature and wave velocity for $MoSi_2$ (ρ ~ 53 %)

T_0 (K)	T_{ad} (K)	T_c (K)	Velocity (mm s^{-1})
298	1913	1615	1.30
373	1961	1798	2.09
473	2029	1884	2.81
573	2099	1974	3.05
673	2173	2046	5.84

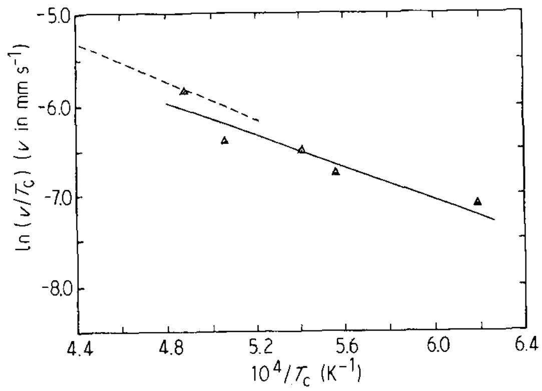

Figure 6 The temperature dependence of the wave velocity in the synthesis of $MoSi_2$. (▲) Present work, (– – –) [9].

data presented in Table III. Also shown in Fig. 6 are results of a previous investigation on the combustion synthesis of $MoSi_2$ [9]. The activation energy calculated from the present investigation, 139.4 kJ mol^{-1}, is in reasonable agreement with that reported by Bloshenko *et al.* [9],167.2 kJ mol^{-1}. However, both of these values are considerably lower than the activation energy reported for the diffusion of Si in Mo [20] or in $MoSi_2$ [21]. Brewer *et al.* [20] reported an activation energy of 183.9 kJ mol^{-1} for the diffusion of Si into Mo (with $MoSi_2$ as a source). The activation energy for the reactive diffusion of Si into $MoSi_2$ is reported to be 240.8 kJ mol^{-1} [21]. It has been suggested by Naiborodenko and Itin [22] that the discrepancy between activation energies from combustion reactions in powders and from diffusion couple experiments may be the consequence of higher defect concentration in the case of powders. In a more recent investigation, Munir and Wang [23] suggested that enhanced reactivity (diffusivity) may be caused by thermal migration. This phenomenon, which occurs in systems with high thermal gradients (as is the case in SHS reactions), can lead to significantly higher levels of point defects at the reaction front and hence enhancement of vacancy-assisted diffusion.

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