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Thermodynamic calculation and an experimental study of the combustion synthesis of $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$)



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ABSTRACT

The theoretical adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$) is calculated. The results indicate that the theoretical adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$ increases with an increasing Nb content when $(Mo_{1-x}Nb_x)Si_2$ is of a single-phase structure, but decreases with an increasing Nb content when $(Mo_{1-x}Nb_x)Si_2$ is of a double-phase structure. All of the temperatures are higher than 1800 K, indicating that $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$) can be prepared by the combustion synthesis method. In this work, $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$) alloys are successfully synthesized by the combustion synthesis process from elemental powders of Mo, Nb, and Si. The highest combustion temperature and combustion product structure are studied. The results confirm that the variation of the experimental maximum combustion temperature of $(Mo_{1-x}Nb_x)Si_2$ is consistent with that of the theoretical adiabatic temperature. The combustion products are non-equilibrium species, and a supersaturated solid solution of C11_b type $(Mo_{1-x}Nb_x)Si_2$ forms during combustion synthesis.

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1. Introduction

Molybdenum disilicide (MoSi₂) is regarded as a promising material for high temperature structural purposes because of its high melting point (2030 °C), good oxidation resistance in elevated temperature (>1600 °C), relatively low density (6.24 g/cm³), and so on [1–3]. Unfortunately, the application of MoSi₂ is limited by low fracture toughness at room temperature (2–3 MPa m^{1/2}) and poor creep resistance at high temperature (i.e., greater than the Brittle–Ductile Transition Temperature).

Approaches to improve the low temperature fracture toughness and high temperature creep properties of $MOSi_2$ have been focused on compositing and alloying. Alloying strategies include the addition of a third element, such as W, Al, Mg, Ge, Re, Nb, Ta, and V [1,4–8]. The calculations based on a first principles approach have suggested that Nb is an ideal alloying element for $MOSi_2$ [5,6]. Waghmare and Harada observed solid-solution softening in $MOSi_2$ alloyed with Nb [5,6]. At room temperature, solid-solution softening leads to compressive plasticity in polycrystalline $MOSi_2$ alloyed with 1 at.% Nb. In addition, at high temperatures (1200– 1600 °C), the yield strengths of Nb-containing alloys may be up to an order of magnitude higher than that of pure $MOSi_2$ [9]. In contrast, silicides with the C40 structure are expected to be potential materials for reinforcing the C11_b MoSi₂ matrix due to the promotion of anomalous strengthening at approximately 1500 °C by the addition of the C11_b-stabilised elements. Thus, NbSi₂/MoSi₂ composites are expected to exhibit a good balance of mechanical properties [10].

Combustion synthesis (self-propagating high-temperature synthesis, SHS) technology is based on the use of a chemical reaction under a certain atmosphere to ignite powder compacts. Combustion synthesis utilizes the heat generated by an exothermic reaction, which becomes self-sustained in the form of a combustion wave after the external ignition [11]. Over 500 compounds have been reported to be synthesized by this method [11–15]. However, only a few reports consider the combustion synthesis of (Mo,Nb)Si₂ alloys.

The adiabatic combustion temperature (T_{ad}) is the highest temperature that an exothermic reaction system can achieve. T_{ad} can directly affect the microstructure and properties of the combustion synthesized products and is the most important thermodynamic parameter to describe the SHS reaction characteristics. Therefore, the calculation of the adiabatic combustion synthesis. Because of the lack of the corresponding thermodynamic data of $(Mo_{1-x}Nb_x)Si_2$, such as ΔH^0_{298} and C_p , it is difficult to calculate the value of T_{ad} . The method of Calculation of Phase Diagrams (CALPHAD) can compute the balance characteristics of the system, such as ΔH^0_{298} and C_p , which allows for the calculation of the







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adiabatic combustion temperature [16,17]. However, it is difficult to find corresponding reports on the calculation of $(Mo_{1-x}Nb_x)Si_2$ alloys.

The two-sublattice model [18,19] was applied to describe the thermodynamic characteristics of $(Mo_{1-x}Nb_x)Si_2$. ΔH^0_{298} , C_p and T_{ad} of the $(Mo_{1-x}Nb_x)Si_2$ system were analysed and calculated using the thermodynamic calculation. The calculation results were compared with the actual experiment results of combustion synthesis.

2. Calculation of the theoretical adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$)

The theoretical adiabatic temperature (T_{ad}) can be used as the qualitative basis to judge whether the combustion reaction can be self-sustaining. On the basis of experimental observations, a system with $T_{ad} > 1800$ K was previously reported to react in a self-propagating mode [20]. T_{ad} can be calculated using formula (1).

$$-\Delta H_{298}^0 = \int_{T_0}^{T_{ad}} C_p dT$$
 (1)

where ΔH_{298}^0 is the standard molar enthalpy of the compound at 298 K, T_{ad} is the theoretical adiabatic temperature of the combustion synthesis reaction, T_0 is the original temperature of the combustion synthesis, and C_p is the molar heat capacity of the combustion synthesis product.

2.1. C11_b-type (Mo_{1-x}Nb_x)Si₂

Fig. 1 shows the schematic phase diagram of the quasi-binary $MoSi_2-NbSi_2$ system [21]. From the figure, a small amount of Nb atoms (x < 0.05) is observed to replace the Mo atoms in the C11_b type $MoSi_2$, and then, linear-stoichiometric compounds of $(Mo_{1-x}Nb_x)Si_2$ with a C11_b crystal structure are formed; the process is described in Eq. (2).

$$(1 - x)Mo + xNb + 2Si \rightarrow (Mo_{1-x}Nb_x)Si_2$$
(2)

In the present work, the C11_b phase was described by a twosublattice model [18,19] $(Mo_{1-x}Nb_x)Si_2$ with Mo and Nb in the first sublattice and Si in the second one, where *x* represents the mole fraction of Nb in the first sublattice. The Gibbs free energy per mol of formula unit C11_b type $(Mo_{1-x}Nb_x)Si_2$ is given by the following expression:



Fig. 1. Schematic phase diagram of the quasi-binary MoSi₂-NbSi₂ system.

$$G_{(Mo_{1-x}Nb_x)Si_2} = (1-x)G_{Mo:Si}^{MoSi_2} + xG_{Nb:Si}^{MoSi_2} + RT[(1-x)\ln(1-x) + x\ln x] + x(1-x)\sum_{j}^{j}L_{Mo,Nb:Si}^{MoSi_2}(1-2x)^j$$
(3)

 $G_{\text{MoSi}_2}^{\text{MoSi}_2}$ and $G_{\text{Nb:Si}}^{\text{MoSi}_2}$ are the molar Gibbs energies of C11_b type MoSi₂ and C11_b type NbSi₂ (the C11_b type NbSi₂ is a hypothetical compound), respectively. ${}^{j}L_{\text{MoNDSi}}^{\text{MoSi}_2}$ (j = 0, 1, 2, ...) is the interaction parameter between Mo and Nb in the first sublattice, while the second sublattice is occupied by Si. $G_{\text{MoSi}_2}^{\text{MoSi}_2}$ and ${}^{j}L_{\text{MoNDSi}}^{\text{MoSi}_2}$ were calculated using the expressions in Table 1 [22].

Substituting the formula into the table for $G_{\text{MoSi}_2}^{\text{MoSi}_2}$, $G_{\text{Nb:Si}}^{\text{MoSi}_2}$ and ${}^{j}L_{\text{Mo,Nb:Si}}^{\text{MoSi}_2}$ in the equation tree, the Gibbs free energy $(G_{(\text{Mo}_{1-x}\text{Nb}_x)\text{Si}_2})$ of C11_b type $(\text{Mo}_{1-x}\text{Nb}_x)\text{Si}_2$ at different temperatures were solved.

In addition, $G_{(Mo_{1-x}Nb_x)Si_2}$ can be calculated using formula (4).

$$G_{(Mo_{1-x}Nb_x)Si_2} = \Delta H^0_{298} - T\Delta S^0_{298} + \int_{298}^{T} C_p dT - T \int_{298}^{T} (C_p/T) dT \qquad (4)$$

The $G_{(Mo_{1-x}Nb_x)Si_2}$ calculated by expression (3) were substituted into formula (4), and then, the equations were developed. The best fit results of ΔH^0_{298} , ΔS^0_{298} and C_p of C11_b type (Mo_{1-x}Nb_x)Si₂ were obtained by solving the equations, which are presented in Table 2.

From Table 2, the entropy value of $(Mo_{1-x}Nb_x)Si_2$ is found to be influenced by the Nb content. Pure $MOSi_2$ has the lowest entropy value of 70.111 J K⁻¹ mol⁻¹. The entropy of $(Mo_{1-x}Nb_x)Si_2$ rapidly increases to 78.140 J K⁻¹ mol⁻¹ when x = 0.01 and then increases slightly with the continuous increase of the Nb content. With the formation of C11_b type $(Mo_{1-x}Nb_x)Si_2$ when the Nb atoms replace some Mo atoms in the C11_b phase, the mixing entropy and vibrational entropy are increased, which is beneficial to the stabilisation of C11_b phase. However, the solid solution of Nb atoms will lead to the crystal lattice distortion, and then cause the increase of crystal energy.

Furthermore, the addition of Nb also causes the change of heat capacity (C_p) of (Mo_{1-x}Nb_x)Si₂. When Nb atoms enter into the lattice of C11_b phase, point defects are formed and additional energy (the vacancy formation enthalpies) must be provided to the crystal, thereby causing the additional specific heat capacity.

The value of ΔH_{298}^0 of $(Mo_{1-x}Nb_x)Si_2$ increases with the addition of niobium. The variation of C_p and ΔH_{298}^0 will inevitably cause the variation of the heat of combustion synthesis reaction, resulting in the change of the adiabatic combustion temperature.

According to the formula (1) and the thermodynamic parameters in Table 2, the adiabatic temperatures of reaction (2) were calculated, as presented in Table 3. The theoretical adiabatic temperature of $C11_b$ type $(Mo_{1-x}Nb_x)Si_2$ is found to be higher than 1800 K and rises with the increase of Nb. The results indicate that $C11_b$ type $(Mo_{1-x}Nb_x)Si_2$ can be synthesized via the combustion synthesis process and that the addition of Nb is beneficial to the combustion synthesis reaction.

2.2. C40-type (Mo_{1-x}Nb_x) Si₂

Fig. 1 illustrates that the $(Mo_{1-x}Nb_x)Si_2$ alloy is composed of a single C40 phase at room temperature when $x \ge 0.25$, while at 1875 K, $(Mo_{1-x}Nb_x)Si_2$ is in the C40 single-phase area when $x \ge 0.22$. Under the adiabatic condition, the combustion wave can sustain itself only when the T_{ad} is higher than 1800 K, indicating that the combustion products are synthesized at temperatures higher than 1800 K. Therefore, the equilibrium compositions of the combustion products should correspond to the equilibrium compositions at high temperature; this thermodynamic calculation of $(Mo_{1-x}Nb_x)Si_2$ was conducted according to the equilibrium compositions at 1873 K. The calculation process of the adiabatic

 Table 1

 Optimized parameters for the phases in the Nb–Si–Mo ternary system.

Phase	Parameters
C11 _b Mo(Nb)Si ₂	$\begin{split} & \text{Model} \; (\text{Mo,Nb})_{0.333} \text{Si}_{0.667} \\ & G_{\text{MoSi}_2}^{\text{MoSi}_2} = -0.333 \text{GHSER}_{\text{Mo}} - 0.667 \text{GHSER}_{\text{Si}} - 43813.1409 - 1.857 \\ & G_{\text{MoSi}_2}^{\text{MoSi}_2} = -0.333 \text{GHSER}_{\text{Nb}} - 0.667 \text{GHSER}_{\text{Si}} - 49,220 + 3.57 \\ & 0L_{\text{Mo,NbSi}}^{\text{MoSi}_2} = -13,000 + 37 \\ & 1L_{\text{Mo,NbSi}}^{\text{MoSi}_2} = -5822.58966 + 1.67 \end{split}$
C40 Nb(Mo)Si ₂	$ \begin{array}{l} \mbox{Model} \ (Mo,Nb)_{0.333} Si_{0.667} \\ G^{C40}_{MoSi} = -0.333 GHSER_{Mo} - 0.667 GHSER_{Si} - 37,900 - 4.211 T \\ G^{MoSi}_{NbSi} = -0.333 GHSER_{Nb} - 0.667 GHSER_{Si} - 51,200 - 5.0T \\ o \ L^{20}_{Mo,NbSi} = -37,500 + 20.16T \\ {}^{1} \ L^{C40}_{Mo,NbSi} = -4000 + T \\ {}^{2} \ L^{C40}_{Mo,NbSi} = -5000 + 1.5T \end{array} $

 $GHSER_{Mo},GHSER_{Si}$ and $GHSER_{Nb}$ are the standard reference states Gibbs free energy of Mo, Si and Nb, respectively.

Table 2

The least-squares solutions to the ΔH^0_{298} , ΔS^0_{298} and C_p of the C11_b (Mo_{1-x}Nb_x)Si₂.

Compounds	$\Delta H^0_{298}/$ kJ mol ⁻¹	$\Delta S^0_{298}/ m JK^{-1}mol^{-1}$	$C_p/\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}$
			$C_p = a + b \times 10^{-3} T$
MoSi ₂	-131.962	70.111	$C_p = 66.192 + 14.525 \times 10^{-3} T$
$(Mo_{0.99}Nb_{0.01})Si_2$	-132.338	78.140	$C_p = 67.459 + 12.364 \times 10^{-3} T$
(Mo _{0.97} Nb _{0.03})Si ₂	-133.015	78.388	$C_p = 67.459 + 12.364 \times 10^{-3} T$
(Mo _{0.95} Nb _{0.05})Si ₂	-133.842	78.475	$C_p = 67.459 + 12.364 \times 10^{-3} \ T$

Table 3

The theoretical adiabatic combustion temperature of C11_b (Mo_{1-x}Nb_x)Si₂.

Compounds	$MoSi_2$	$(Mo_{0.99}Nb_{0.01})Si_2$	$(Mo_{0.97}Nb_{0.03})Si_2$	(Mo _{0.95} Nb _{0.05})Si ₂		
$T_{\rm ad}/{\rm K}$	1904	1927	1935	1944		

Table 4

The least-squares solutions to the ΔH_{298}^0 and C_p of the C40 (Mo_{1-x}Nb_x)Si₂.

Compound	$\Delta H_{298}^0/\mathrm{kJ}~\mathrm{mol}^{-1}$	$C_p/\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}$
(Mo _{0.78} Nb _{0.22})Si ₂	-130.000	$C_p = 66.4706 + 14.0498 \times 10^{-3} T$
(Mo _{0.75} Nb _{0.25})Si ₂	-131.845	$C_p = 66.5086 + 13.9849 \times 10^{-3} T$
(Mo _{0.65} Nb _{0.35})Si ₂	-137.104	$C_p = 66.635 + 13.769 \times 10^{-3} T$
(Mo _{0.55} Nb _{0.45})Si ₂	-141.583	$C_p = 66.762 + 13.553 \times 10^{-3} T$
(Mo _{0.2} Nb _{0.8})Si ₂	-152.07	$C_p = 67.206 + 12.796 \times 10^{-3} T$
NbSi ₂	-154.152	$C_p = 67.460 + 12.364 \times 10^{-3} T$

temperature of C40-type $(Mo_{1-x}Nb_x)Si_2$ is consistent with that of C11_b-type $(Mo_{1-x}Nb_x)Si_2$, and the simulation results of ΔH^0_{298} and C_p of C40-type $(Mo_{1-x}Nb_x)Si_2$ are listed in Table 4. The ΔH^0_{298} of C40-type $(Mo_{1-x}Nb_x)Si_2$ are observed to increase significantly with the increase of Nb, which is beneficial to the combustion synthesis reaction. Based on the data in Table 4, the adiabatic temperature of C40-type $(Mo_{1-x}Nb_x)Si_2$ can be solved.

Fig. 2 shows the relationship between T_{ad} of $(Mo_{1-x}Nb_x)Si_2$ and the amount of Nb content (*x*). The values of T_{ad} of $(Mo_{1-x}Nb_x)Si_2$ $(0 \le x \le 1)$ are all higher than 1800 K, indicating the feasibility of the combustion reaction. The adiabatic temperature of pure $MoSi_2$ (1904 K) is the lowest of the C11_b phase. The value of T_{ad} of C11_b-type $(Mo_{1-x}Nb_x)Si_2$ increases with the increase of the solid-solution of Nb and reaches the maximum (1944 K) at the junction between the single-phase region (C11_b-phase) and the



Fig. 2. The adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$.

two-phase region (C11_b-phase and C40 phase). The adiabatic temperature of pure NbSi₂ (2163 K) is the highest of the whole system. With the formation of the C40 type ($Mo_{1-x}Nb_x$)Si₂ when Mo atoms enter into the lattice of NbSi₂, T_{ad} decreases with the increase of Mo and reaches the minimum (1887 K) at the junction between the C40-phase region and the two-phase region.

When $0.05 \le x < 0.22$, $(Mo_{1-x}Nb_x)Si_2$ is composed of the C11_b phase and the C40 phase at 1873 K; in this case, the adiabatic temperature depends on the relative amount and the values of T_{ad} of both phases. In the two-phase region, the value of T_{ad} of the C11_b phase is relatively high (1944 K), while that of the C40 phase is relatively low (1887 K). With the increase of Nb content, the quantity of C40 phase increases, while that of C11_b phases decreases. As a result, the reaction heat of the $(Mo_{1-x}Nb_x)Si_2$ system reduces, leading to the linear decrease of T_{ad} .

3. Combustion synthesis of $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$)

3.1. Experimental procedure

Molybdenum (3–5 μ m, 99.9% purity), silicon (<74 μ m, 99.5% purity) and niobium (<48 μ m, 99.8% purity) powders were used as the starting materials. Powder mixtures were prepared with fourteen different nominal compositions, as listed in Table 5. The mixed powders were cold-pressed at 200 MPa of applied pressure into cylindrical compacts. The relative density of compacts was approximately 55% of the theoretical density.

The combustion synthesis experiments were conducted in a steel combustion chamber with a glass window, under an atmosphere of pure argon (99.99%, 0.1 MPa). The ignition was accomplished by a heated molybdenum coil at 20 V and 25 A at room temperature.

A thermocouple wire (WRe3–WRe25 with a diameter of 0.1 mm) was placed inside a small hole drilled in the bottom of

Table 5Sample number and nominal composition of $MoSi_2$ alloyed Nb.

No.	The nominal composition	No.	The nominal composition
N0	MoSi ₂	N7	(Mo _{0.75} Nb _{0.25}) Si ₂
N1	(Mo _{0.97} Nb _{0.03}) Si ₂	N8	(Mo _{0.7} Nb _{0.3}) Si ₂
N2	(Mo _{0.94} Nb _{0.06}) Si ₂	N9	(Mo _{0.65} Nb _{0.35}) Si ₂
N3	(Mo _{0.91} Nb _{0.09}) Si ₂	N10	(Mo _{0.6} Nb _{0.4}) Si ₂
N4	(Mo _{0.88} Nb _{0.12}) Si ₂	N11	(Mo _{0.55} Nb _{0.45}) Si ₂
N5	(Mo _{0.85} Nb _{0.15}) Si ₂	N12	(Mo _{0.5} Nb _{0.5}) Si ₂
N6	(Mo _{0.8} Nb _{0.2}) Si ₂	N13	NbSi ₂

the powder compacts to record the combustion synthesis temperature with a frequency of 300 Hz.

The combustion products were analysed using a scanning electron microscope (S-3400N) with EDX analysis (EX-250, HORIBA). The phase composition was investigated using a Rigaku D/Max-3B X-ray diffractometer (XRD) using a Cu Ka (λ = 0.15406 nm) radiation operating at 35 kV and 30 mA.

3.2. Phase structure of the combustion products

Fig. 3 shows the SEM micrographs of the fracture surfaces of the combustion products. Fig. 3a and b shows the microstructures of $MoSi_2$ and $(Mo_{0.85}Nb_{0.15})Si_2$, respectively. The fracture surface of the combustion products displays porous material characteristics. Additionally, both samples are composed of spherical particles.

The XRD spectrums of the combustion products are shown in Fig. 4. The molybdenum disilicide with C11_b crystal structure is observed to be the only phase in the SHS products of the N0 sample. Additionally, the products of the $(Mo_{0.97}Nb_{0.03})Si_2$ and $(Mo_{0.94}Nb_{0.06})Si_2$ specimens remain a single C11_b phase structure, and no diffraction peaks corresponding to Nb containing phases are observed; these observations indicate that all of the Nb atoms substitute for Mo atoms in MoSi₂ during the SHS. These results indicate that Nb alloyed MoSi₂ is synthesized by SHS in this work.

When x = 0.09, very weak diffraction peaks of NbSi₂ and C40type MoSi₂ appear. From the partial magnified image of Fig. 4d (upper-part of Fig. 4), the diffraction peak of the C40 NbSi₂ phase is obviously present in the (Mo_{0.91}Nb_{0.09})Si₂ specimen. With the increase of niobium, the intensity of the NbSi₂ diffraction peaks gradually strengthens, whereas the diffraction peaks of MoSi₂ begin to weaken. However, the main phase in all specimens (except N13) continues to be C11_b MoSi₂. When x = 1, the niobium disilicide with C40 crystal structure is the only phase in the SHS products of N13 sample.



Fig. 3. SEM micrographs of the fracture surface of the combustion products.

Fig. 5 compares the phase compositions of the combustion products and the equilibrium phase constituents of the quasi-binary phase diagram (see Fig. 1). As for the equilibrium phase (see the upper bar in Fig. 5), $(Mo_{1-x}Nb_x)Si_2$ is C11_b structure when x < 0.05, and possesses $C11_b/C40$ duplex phase when $0.05 \le x \le 0.22$, then is C40 structure when $x \ge 0.22$. While in the combustion products (see the lower bar in Fig. 5), $(Mo_{1-x}Nb_x)Si_2$ is C11_b structure when x < 0.09, and keeps being C11_b/C40 duplex phase after that. It can be seen that the phase compositions of the combustion products are quite different with the equilibrium phase constituents. The critical value between the C11_b field and C11_b/C40 duplex phase field rises from 0.05 to 0.09; it means that the solid solubility of Nb in C11_b phase is much higher in the combustion products. In addition, C11_b-type MoSi₂ still remains in the combustion products when $0.22 \le x \le 0.5$, which is also inconsistent with the equilibrium phases.

Zhang et al. [23] and Zhang et al. [24] prepared a series of $(Mo_{1-x}Nb_x)Si_2$ alloys via the arc-melting process; they found that the C40 phase was the main phase when x = 0.06 and became the only phase in the alloy when $x \ge 0.2$. Harada et al. [6] also prepared $(Mo_{1-x}Nb_x)Si_2$ alloys via the arc-melting process. The results indicated that the alloy was $C11_b$ single-phase when x < 0.039 and became a single C40 phase when $x \ge 0.18$, which is consistent with the equilibrium microstructure. However, when $(Mo_{1-x}Nb_x)Si_2$ alloys were prepared via the self-propagating high temperature synthesis, Maglia et al. [25] found that the C40 phase did not appear when $x \le 0.1$ and that the C11_b phase remained being the major part of the alloy till x = 0.2. These results are similar to our work.

Because of the extremely high reaction velocity, high combustion temperature and acute temperature variation, the combustion synthesis of Mo–Si–Nb alloy is a non-equilibrium reaction process. Therefore, the combustion products are also non-equilibrium in nature. A supersaturated solid solution of C11_b type $(Mo_{1-x}Nb_x)Si_2$ is synthesized. Because arc-melting is a melting and solidification process, to obtain better homogeneity, it often undergoes the turning and melting cycle for 5–6 times. Therefore, the arc-melted alloys are similar to the equilibrium microstructure.

3.3. The highest temperature of the combustion synthesis

Table 6 shows the calculated and experimental maximum combustion temperature of $(Mo_{1-x}Nb_x)Si_2$, and Fig. 6 exhibits the trend curve of temperature with the Nb content. As shown in Fig. 6, the trend of the highest combustion temperature is consistent with that of the theoretical adiabatic temperature. However, the observed combustion temperature is always lower than the calculated temperature, e.g., T_{ad} of MoSi₂ is 1904 K, while the actual maximum combustion temperature of MoSi₂ is 1695 K. This difference is due to the mass or energy loss in the experiments, because of the combustion synthesis reactions are usually conducted under non-adiabatic conditions.

The theoretical adiabatic temperature is the maximum temperature achieved under adiabatic conditions. In fact, the density of green compacts, atmosphere, preheating temperature, and so on would influence the actual combustion temperature. The combustion temperature of MoSi₂ measured by Zhang and Munir was only 1615 K [26]. Yeh and Chen reported the temperature to be 1713 K [27], which is close to the results of this work. Deevi found that the combustion temperature of MoSi₂ was 1886 K under argon atmosphere and 1690 K under vacuum [28]. However, Xu et al. reported the combustion temperature to be 1796 K under argon atmosphere and 1871 K under vacuum [29]. All of the experimental combustion temperatures are observed to be lower than the theoretical adiabatic temperature.



Fig. 4. XRD analyses of $MoSi_2$ alloyed with Nb via combustion synthesis.



Fig. 5. The phase composition of $(Mo_{1-x}Nb_x)Si_2$ with different values of *x*.

The thermodynamic calculation indicates that the solid solution of Nb in MoSi₂ can promote the exothermic reaction, causing the value of T_{ad} of $(Mo_{1-x}Nb_x)Si_2$ to increase with the increasing Nb content, reaching a maximum at the solid solubility limit (x = 0.05). The experimental highest temperature also increases with the addition of Nb. However, when x > 0.05, the highest temperature still increases with the Nb content and reaches the maximum at 0.09. The analysis of XRD indicates that the C11_b phase is the only phase when $x \le 0.06$, only trace C40 phase is identified when x = 0.09, and the supersaturated solid solution of C11_b phase is synthesized when x > 0.05. These results indicated that the supersaturated solution of Nb in C11_b phase can further promote the heat release of reaction, causing the maximum combustion temperature continue to increase when x > 0.05.

Table 6

The adiabatic temperature (T_{ad}) and the experimental highest combustion temperature of $(Mo_{1-x}Nb_x)Si_2$.

x value in $(Mo_{1-x}Nb_x)Si_2$	0	0.01	0.03	0.06	0.09	0.12	0.15	0.2
T _{ad}	1904	1927	1935	1942	1937	1931	1926	1916
Experimental temperature	1696	-	1773	1788	1858	1813	1778	1743
x value in $(Mo_{1-x}Nb_x)Si_2$	0.25	0.3	0.35	0.4	0.45	0.5	0.55	1
T _{ad}	1907	1938	1966	1992	2015	2037	2058	2163
Experimental temperature	1713	1813	1860	1889	1828	1857	-	1949



Fig. 6. The variation of the adiabatic temperature and the experimental highest combustion temperature with the Nb content.

When *x* increases from 0.09 to 0.25, the maximum combustion temperature decreases with the increasing niobium content and reaches a valley value at 0.25. In addition, the variation trend is similar to that of the theoretical adiabatic temperature. According to the XRD results, NbSi₂ appears when *x* = 0.09 and increases with the addition of Nb. As shown in the thermodynamic calculation results, the T_{ad} of the NbSi₂ phase is relatively low (1907 K) when $0.05 \le x < 0.22$, causing the T_{ad} of the system to decrease with the increase of NbSi₂. This behaviour is also the reason for the decrease of the combustion temperature when $0.09 \le x < 0.25$; also, the difference between the composition range is caused by the supersaturated solution of Nb in C11_b phase.

When x > 0.25, $(Mo_{1-x}Nb_x)Si_2$ is composed of the single C40 phase in the equilibrium phase diagram and the value of T_{ad} of $(Mo_{1-x}Nb_x)Si_2$, which is also similar to the maximum combustion temperature, increases with the increasing Nb content. In addition, the calculation results indicate that the theoretical adiabatic temperature of C40-type $(Mo_{1-x}Nb_x)Si_2$ increases with the Nb content. This result indicates that although the combustion products are composed of C40 phase and C11_b phase in this composition range, the Nb content in C40 phase begins to increase, resulting in the increase of the combustion temperature.

Although the combustion temperature of disilicide is changed with the addition amount of niobium, the combustion mode may not be changed. All the combustion temperatures are higher than the melting point of silicon (1685 K) but lower than the melting point of molybdenum (2890 K) and niobium (2741 K), causing Si melts firstly. Solid Mo and Nb particles are wetted by the molten Si and begin to dissolve into the liquid. When the liquid phase becomes supersaturated with solid phases, combustion products will precipitate [30,31].

4. Conclusions

- (1) Using the two-sublattice model and based on thermodynamics calculation, the theoretical adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$ was calculated. The results indicate that $(Mo_{1-x}Nb_x)Si_2$ ($0 \le x \le 1$) alloys can be synthesized via the combustion synthesis reaction with Mo, Si and Nb elemental powders. The experimental combustion products are nonequilibrium structures. A supersaturated solid solution of C11_b type $(Mo_{1-x}Nb_x)Si_2$ forms when x > 0.05.
- (2) The solid solution of Nb can change the thermal capacity and the enthalpy of the C11_b phase and the C40 phase, resulting in the change of the theoretical adiabatic temperature. The theoretical adiabatic temperature of $(Mo_{1-x}Nb_x)Si_2$ increases when *x* rises from 0 to 0.05, and decreases when *x* rises from 0.05 to 0.22, then increases again with the further increase of Nb content. The trend of the experimental maximum combustion temperature of $(Mo_{1-x}Nb_x)Si_2$ is consistent with that of the theoretical adiabatic temperature.

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References

- J.J. Petrovic, Toughening strategies for MoSi₂-based high temperature structural silicides, Intermetallics 8 (2000) 1175–1182.
- [2] P. Feng, W. Liu, A. Farid, J. Wu, J. Niu, X. Wang, Y. Qiang, Combustion synthesis of (Mo_{1-x}, Cr_x)Si₂ (x = 0.00–0.30) alloys in SHS mode, Adv. Powder Technol. 23 (2012) 133–138.
- [3] Z. Wu, W. Zhou, F. Luo, D. Zhu, Effect of MoSi₂ content on dielectric and mechanical properties of MoSi₂/Al₂O₃ composite coatings, Trans. Nonferrous Met. Soc. 22 (2012) 112–116.
- [4] A.J. Heron, G.B. Schaffer, Mechanical alloying of MoSi₂ with ternary alloying elements. Part 1: experimental, Mater. Sci. Eng. A352 (2003) 105–110.
- [5] U.V. Waghmare, V. Bulatov, E. Kaxiras, M.S. Duesbery, Microalloying of ductility in molybdenum disilicide, Mater. Sci. Eng. A 261 (1999) 147–157.
- [6] Y. Harada, Y. Murata, M. Morinaga, Solid solution softening and hardening in alloyed MoSi₂, Intermetallics 6 (1998) 529–535.
- [7] R. Mitra, R. Khana, V.V. Rama Rao, Microstructure, mechanical properties and oxidation behavior of a multiphase (Mo, Cr)(Si, Al)₂ intermetallic alloy-SiC composite processed by reaction hot pressing, Mater. Sci. Eng. A 382 (2004) 150–161.
- [8] A. Shan, F. Wei, H. Hashimoto, Y.H. Park, Effect of Mg addition on the microstructure and mechanical properties of MoSi₂ alloys, Scr. Mater. 46 (2002) 645–648.
- [9] A.A. Sharif, A. Misra, T.E. Mitchell, Deformation mechanisms of polycrystalline MoSi₂ alloyed with 1 at.% Nb, Mater. Sci. Eng. A358 (2003) 279–287.
- [10] K. Hagihara, T. Nakano, S. Hata, O. Zhu, Y. Umakoshi, Improvement of aligned lamellar structure by Cr-addition to NbSi₂/MoSi₂ duplex-silicide crystals, Scr. Mater. 62 (2010) 613–616.
- [11] J.J. Moore, H.J. Feng, Combustion synthesis of advanced materials: Part I. Reaction parameters, Prog. Mater. Sci. 39 (1995) 243–273.
- [12] J.J. Moore, H.J. Feng, Combustion synthesis of advanced materials: Part II. Classification, applications and modeling, Prog. Mater. Sci. 39 (1995) 275–316.
- [13] J.K. Tien, G.E. Vignoul, M.W. Kopp, Materials for elevated-temperature applications, Mater. Sci. Eng. A 143 (1991) 43–49.

- [14] J.H. Perepezko, The hotter the engine, the better, Science 326 (2009) 1068–1069.
- [15] E. Summers, A.J. Thom, B. Cook, M. Akinc, Extrusion and selected engineering properties of Mo–Si–B intermetallics, Intermetallics 8 (2000) 1169–1174.
- [16] Y. Liu, S. Yin, W. Zhang, H. Lai, Thermodynamic analysis of the self-propagation high-temperature synthesis Al₂O₃/B₄C composite, Scr. Mater. 39 (1998) 1237– 1242.
- [17] Y. Liu, S. Yin, W. Zhang, H. Lai, Application of CALPHAD technique in thermodynamic analysis of combustion synthesis of multi phase ceramics, Chin. J. Rare Met. 24 (1) (2000) 37–41.
- [18] B. Sundman, J. Ågren, A regular solution model for phases with several components and sublattices, suitable for computer applications, J. Phys. Chem. Solids 42 (1981) 297–301.
- [19] C. Guo, C. Li, P.J. Masset, Z. Du, A thermodynamic description of the Al-Mo-Si system, CALPHAD 36 (2012) 100–109.
- [20] Z.A. Munir, U. Anselmi-tamburini, Self-propagating exothermic reactions: the synthesis of high-temperature materials by combustion, Mater. Sci. Rep. 3 (1989) 277–365.
- [21] T. Geng, C. Li, X. Zhao, H. Xu, C. Guo, Z. Du, Experimental study on the as-cast solidification of the Si-rich alloys of the Nb–Si–Mo ternary system, Intermetallics 18 (2010) 1007–1015.
- [22] T. Geng, C. Li, X. Zhao, H. Xu, Z. Du, C. Guo, Thermodynamic assessment of the Nb–Si–Mo system, CALPHAD 34 (2010) 363–376.

- [23] L.Q. Zhang, W. Du, K.M. Pan, J.P. Lin, G.L. Chen, Effect of alloying on fracture toughness of MoSi₂ at ambient temperature, Heat Treat. Metal. 34 (8) (2009) 31–35.
- [24] F. Zhang, L. Zhang, J. Yu, J. Wu, A comparison of the oxidation behaviors of poly-crystalline and single crystalline NbSi₂ at 1023 K, Acta Metall. Sin. 41 (2005) 645–648.
- [25] F. Maglia, C. Milanese, U. Anselmi-Tamburini, Z.A. Munir, Self-propagating high-temperature synthesis microalloying of MoSi₂ with Nb and V, J. Mater. Res. 18 (2003) 1842–1848.
- [26] S. Zhang, Z.A. Munir, Synthesis of molybdenum silicides by the selfpropagating combustion method, J. Mater. Sci. 26 (1991) 3685–3688.
- [27] C.L. Yeh, W.H. Chen, Combustion synthesis of MoSi₂ and MoSi₂-Mo₅Si₃ composites, J. Alloys Comp. 438 (2007) 165–170.
- [28] S.C. Deevi, Self-propagating high-temperature synthesis of molybdenum disilicide, J. Mater. Sci. 26 (1991) 3343–3353.
- [29] J. Xu, H. Zhang, J. Yan, B. Zhang, W. Li, Effect of argon atmosphere on the formation of MoSi₂ by self-propagating combustion method, Int. J. Refract. Met. Hard Mater. 480 (2009) 315–320.
- [30] F. Baras, D.K. Kondepudi, F. Bernard, Combustion synthesis of MoSi₂ and MoSi₂-Mo₅Si₃ composites: multilayer modeling and control of the microstructure, J. Alloys Comp. 505 (2010) 43–53.
- [31] S.W. Jo, G.W. Lee, J.T. Moon, Y.S. Kim, On the formation of MoSi₂ by selfpropagating high-temperature synthesis, Acta Mater. 44 (1996) 4317–4326.