Self-Propagating High-Temperature Synthesis of Porous Molybdenum Disilicide Composites

M. Malekjafarian [1*], **E. Zahabi** [2], **S.K. Sadrnezhaad** [3]

1,2- Materials Research Group, Iranian Academic Center for Education, Culture and Research (ACECR), Mashhad Branch, P.O. Box 91775-1376, Azadi Square, Mashhad, Iran

3- Department of Materials Science and Engineering, Sharif University of Technology, Azadi Ave., PO Box 11365-9466, Tehran, Iran

* malekjafariyan@gmail.com

Abstract

Microwave processing combined with combustion synthesis was used to fabricate intermetallic composite foam. Internal microwave heating initiated ignition at center of the sample and combustion wave front propagated radially outwards. Open-cell porous $MoSi_2$ intermetallics with adjustable pore characteristics were successfully produced from MoO_3, SiO_2, Mg and C raw materials. Manipulating volume fraction and particle size of the utilized carbon, porosity and pore size of $MoSi_2$ intermetallics were easily controlled. Their values were in the ranges of 18-56% and 0.4-2.0 mm, respectively. From thermodynamic analyses of $MoO_3–xMg–yC$ system, optimal ranges of x and y coefficients were so found to ensure complete reduction of MoO_3 to metallic molybdenum. The influence of x and y values on the process parameters like temperature, front propagation velocity, phase composition and the structure of products were experimentally investigated.

Keywords: *Metal Foam; Composite materials; SHS process; Molybdenum Disilicide.*

Introduction

Microwave heating is fundamentally different from conventional heating. With microwave energy the heat is generated internally through material-microwave interaction instead of originating from an external heating source. This internal volumetric heating results in thermal gradients that are the reverse of" those observed in conventional heating. Consequently, microwave processing makes it possible to heat both small and large shapes very rapidly and relatively uniformly. Silicides of various metals have been the focus of numerous investigations because of their attractive high temperature properties [1–4]. The technological attraction comes mainly from new aerospace needs for high temperature structural materials with properties that cannot be met by ceramics or by conventional superalloys [5,6]. $MoSi_2$ intermetallic compound possesses low density (6.3 g×cm−3), high melting point (2030∘C) and excellent oxidation resistance at elevated temperatures [7,8]. $MoSi_2$ is a dimorph phase: the tetragonal C11b type α-

MoSi2 (low temperature phase) phase is stable up to 1900 oC; above this temperature, α-$MoSi_2$ is transformed into the hexagonal C40-type α-$MoSi_2$ (high temperature phase) phase. This high temperature phase melts in a congruent form at 2020 oC [9]. Several processing routes have been introduced for fabrication of $MoSi_2$ based composites including: hot pressing, reaction bonding, combustion synthesis, infiltration and mechanical alloying [10]. Mechanical alloying (MA) is basically a dry and high energy ball milling process which has been used to synthesize alloys, oxide-dispersion-strengthened alloys, amorphous alloys, various intermetallics compounds, etc. [11,12]. Several studies have been performed on the synthesizing of MoSi2 composites with different second phases such as: Ta, Nb, W, ZrO_2, SiC, Si_3N_4, WSi_2, Mo_5Si_3, TiB_2, Al_2O_3, etc. [13–15]. Molybdenum and Mo-based materials are widely used in many industries (metallurgy, aerospace, electrical industry, electronics, etc.) for the excellent mechanical, thermal and electrical properties

Good corrosion resistance [16–24]. The widespread method for the preparation of molybdenum is the reduction of MoO3 by hydrogen [18,21,25–29]. It was shown [25,28] that two-stage reduction starts at 550 ∘C. At the first stage $MoO_3{\rightarrow}MoO_2$ transformation takes place via Mo_4O_{11} intermediate oxide. At the second stage, MoO_2 converts to Mo at 1000–1100 ∘C. The reduction temperature may be lowered down to 800 ∘C using nano sized MoO_3 [26].

Other distinguished method is the metallo thermic reduction of molybdenum oxide [17,31]. Aluminum seems to be suitable reducer rather than calcium because of lower cost and higher heat of reduction per mole of MoO_3. Although aluminum has more tendencies to reduce MoO_3 than silicon, Al–Si mixture provides more molybdenum yields than pure aluminum [32]. Average conversion at 1200 ∘C was 92%. Carbon is also used to reduce MoO_3 by the $MoO_3 + 3C = Mo + 3CO$ reaction. The Gibbs energy change (ΔGo) of that reaction makes about 270 kJ/mol and usually it is performed at high temperatures 600–1200 ∘C [33,34]. Therefore, an alternative inexpensive and simple method for producing molybdenum powder is of considerable interest. One possible approach is to prepare molybdenum powder by the combustion synthesis (CS) or self-propagation high-

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1. mentor
2. Second author position or job title, Fax and Tel. numbers, and email address (corresponding author)
3. Professor, Department of Materials Science and Engineering, Sharif University of Technology

temperature synthesis (SHS) method [35–37]. SHS is an effective, low-cost method for production of various industrially useful materials including metallic powders [38–40]. Advantages of the SHS in comparison with conventional methods for metal powder production are low energy consumption for achieving high temperatures, high rates of conversion, the simplicity of equipment used and high quality of final products.

It is worth to note that the self-sustaining reduction of MoO3 by magnesium is characterized by high values of ΔGo (−1040 kJ/mol), enthalpy ΔHo (−1060 kJ/mol) and reaction temperature (about 3000 °C). At these temperatures significant amount of initial reactants evaporates. The process proceeds in a violent uncontrollable regime. In order to soften the process conditions the reduction temperature should be decreased significantly. The partial substitution of magnesium for carbon will enable to perform MoO_3 reduction under the controlled self-sustaining regime. It is believed that the key factor to govern the reaction conditions (e.g. thermal regime) is amounts of reducers in the mixture. An additional benefit of using Mg–C reducing mixture is high yield of molybdenum powder due to the low content of the formed MgO. As a result subsequent leaching process of Mo powder will be significantly simplified. The objective of the present research is studying the feasibility of foam production by reaction of the MoO_3–SiO_2–Mg–C mixtures yielding the molybdenum powder.

Experimental procedure

The raw materials used in the SHS for fabrication of the composite foam were Molybdenum oxide (MoO_3) (< 160 μm), Mg (< 45 μm) and graphite (< 45 μm) powders. The powders were evenly blended in a mixer at the molar ratios (quantities of X in Eq. 1) ranging from Y = 0 to Y = 2.5. A green mixture of the reactants was homogenized in a ceramic mortar for 10 min. The blended powder was then cold-pressed by constant compacting pressure 500 MPa in a cylinder (h = 50 mm, ID = 15 mm) to make a precursor. Cylindrical samples with 15mm in diameter and height of 15mm were prepared from the green mixtures with 500MPa pressure. Experiments were carried out in a laboratory constant-pressure microwave in pressure atmosphere. Combustion was initiated by means of a Fe wire located on the below surface of the sample. Fig. 1 shows a schematic outline for the SHS synthesis of porous $MoSi_2$ composite.
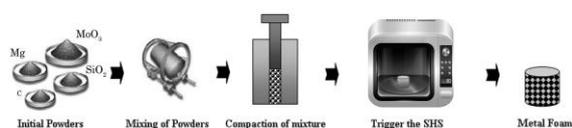

Fig. 1. Schematic illustration of the SHS process for the synthesis of porous molybdenum disilicide composite.

The combustion products were studied by XRD analysis with monochromatic CuKα radiation (diffract meter DRON-3.0). SEM (Philips microscope) analysis was conducted to study the microstructure of combusted samples and washed powders. Reaction that was used was as follows:

$$MoO_3 + (7-X)Mg + (Y)C + 2SiO_2 \rightarrow MoSi_2 + (7-X)MgO + (Y)CO \tag{1}$$
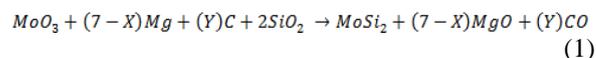
In reaction (1) the value of Y was changed from 0 to 2.5 mol. At each step the amount of C increased for 0.5 mol.

Results and discussion

Thermodynamic consideration

One of the primary tasks to design the combustion synthesis system successfully is to carefully consider the thermodynamics. For estimating the value of adiabatic combustion temperature (Tad) and equilibrium composition of the final products, preliminary thermodynamic analyses of the MoO3(7–x) Mg-yC system were performed using the "ISMAN–THERMO" software developed for multi component hetero phase systems. Calculation of equilibrium characteristics is based on the minimization of the Gibbs free energy of the system, which accounts for the contributions of Gibbs free energies for all components and their concentrations. Firstly, calculations for MoO3(7–x)Mg-yC mixtures (where x and y molar coefficients were varied from 1 to 2 and 0.8 to 2.1, respectively) were performed at 2MPa. The results are shown in Fig. 2a, where Tad is presented as a function of x and y values. According to the results, three areas in the diagram may be marked out. At small amounts of magnesium and carbon Tad is calculated to be in the range of 1300–2100 °C (I area). Here main products of the reaction are Mo, MgO, MoO_2, CO and CO_2. In the II area the products contain Mo, MgO and carbon oxides. Tad is in the range of 1700 to 2500 °C.

For the III area the temperature changes from 1500 to 2700 °C. In this case the products contain Mo, MgO, carbon oxides and molybdenum carbides (Mo_2C and MoC). The calculation shows that CO is the major compound in the gaseous products. To determine pressure influence on Tad and products compositions similar calculations were performed with optimized x and y values (II area in Fig. 2). The results suggest (not shown) that the optimal pressure to obtain solid products containing Mo and MgO is 1.5 MPa. At lower pressures significant amounts of MoO2 may be formed too. Fig. 2b shows the relationship between X and the Tad of the system. Considering the Merzhanov criterion (Tad ≥ 1800 K), this figure implies that the SHS reaction would be stable, only if X is less than 2.5.

SHS reaction, porosity content and morphology

The difference between the severities of the reactions that took place in the different compacts confirmed that the combustion behavior of the reactant
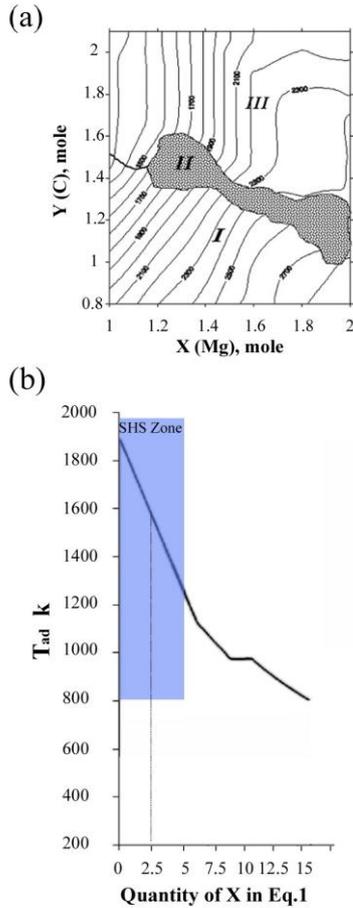

(a)

(b)

Fig. 2. a) Thermodynamic analysis of the MoO_3–xMg–yC system: I area—Mo, MgO, MoO_2, II area—Mo, MgO and III area—Mo_2C, MoC, Mo, MgO.b) The relationship between the blending ratio X (in Eq. 1) and the theoretical adiabatic temperature of the system.

compact varied with C content of the initial powder mixture. Fig. 3 shows the typical SHS sequence of a compact (produced with a compacting pressure of 500 MPa) where in the molar ratio of MoO_3 : Mg : C. It is evident that upon ignition, a distinct reaction front formed and then harshly propagated downwards in a self-sustaining fashion. The severity of the reaction was too high and all the products of the reaction were vaporized. This was attributed to the high adiabatic temperature evolved during the phase transformation. As also revealed in Fig. 3, the combustion front traversed the entire sample in about 4.1 s.

The severity of the reaction was moderated by introducing C in the reactant mixture. When the C content increased to 2.5 mol, as depicted in Fig. 3, the sample compact almost retained its original shape throughout the SHS process. This implied that the reactions evolved less adiabatic temperature in the C-containing compact. Moreover, the addition of C also

led to a slower propagation of the reaction front. As seen in Fig. 3, it took about 7.4 s for the combustion
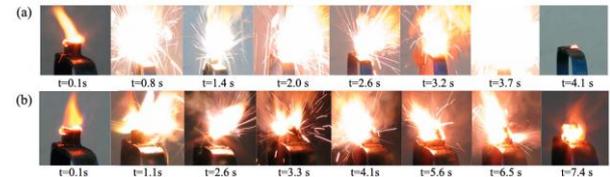

Fig. 3 Recorded images of the combustion reactions of the precursors with different blending ratios of (a) Y = 0.5, (b) Y = 2.5.

wave to arrive to the bottom of the sample. Further experiments with C contents of between Y = 2.5 and Y = 5 confirmed a critical C content of Y=2.5, after which the combustion reaction could not propagate sustainably. This C content (according to Fig. 4) is corresponding to an adiabatic temperature of about 1700 0C.

The C content of the precursor also influenced the porosity content and the morphology of the pores produced during the reactions. Fig. 4 shows the porosity content of the products which were produced with a compacting pressure of 500 MPa and different blending ratios of between Y=0 and Y=2.5. This parameter controls the fraction of the gaseous phase (CO), which influences the porosity formation during the combustion process, and as it can be seen in this figure, the porosity content of the products increased from 18 to 56 percent as the blending ratio increased from X=0.5 to Y= 2.5. The appearance and the pore morphologies of the combustion synthesized MoSi2–MgO foams with different blending ratios (Y=0.5, 1, 1.5, 2 and 2.5) are shown in Fig. 4. This figure shows that when the C content of the precursor was low (Y=0.5, Fig. 4) the precursor deformed considerably during the SHS process and the pores were produced with a closed morphology and the sample deformed, whereas, a precursor with a blending ratio of Y=2 deformed much less and the morphology of the pores formed during the reaction changed from closed to open pores (Fig. 4).
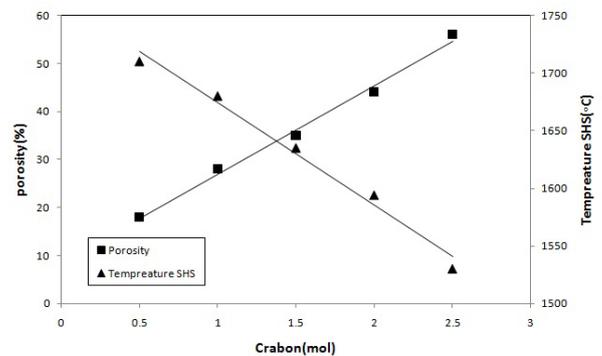

Fig. 4. The porosity content and temperature of the combustion synthesized specimens with different blending rations of between Y=0.5 and Y=2.5.
SEM images of sample 6 after washing in the hydrochloric acid.

very high, the actual temperature of the reaction front should be lower than the theoretical adiabatic temperature due to the heat conduction away from it.

Fig. 5a shows the microstructure of MoSi2 foam specimen and Fig. 5b shows the secondary electron SEM micrograph of the polished surface of a combustion synthesized specimen, the precursor of which was produced using a blending ratio of Y=2.5 and a compacting pressure of 500 MPa. The EDX studies (Fig. 5c,d) showed that the microstructure consisted of MoSi2 particle crystals and MoSi2 amorphous phase.

SEM images prove this claim that Because of high temperature combustion synthesis reaction, very high speed cooling large amounts of reaction product becomes amorphous structure.

As seen in Fig. 5b the amount of amorphous MoSi2 crystals MoSi2 has also been formed. Maximum temperature is reduced by increasing the amount of carbon. The reason is that more carbon monoxide gas was produced. Therefore, this gas can be removed the heat. As metallographic pictures show that an increased amount of carbon caused by product was synthesized by an increase in cavities.

Conclusions

Molybdenum disiliside composite foam was successfully fabricated by the Self-propagating High-temperature Synthesis of MoO3, mg and C powders, and the following results were obtained:

1. The SEM results showed that MoSi2 (mainly α phase) intermetallic compound with amorphous structure can be successfully produced by SHS from initial elemental powders.
2. The molar blending ratio of the green ingredients was found to be an important parameter controlling the behavior of the SHS reaction, the porosity content of the final product, and the morphology of the pores produced.
3. The critical molar powder ratio to produce open pores through a sustainable SHS reaction was found to be Y = 2.5.
4. The product structure was amorphous Because of high cooling rate.
5. The metallographic images showed that heterogeneous distribution of pores in the product synthesized by the reaction of the material is uniform.
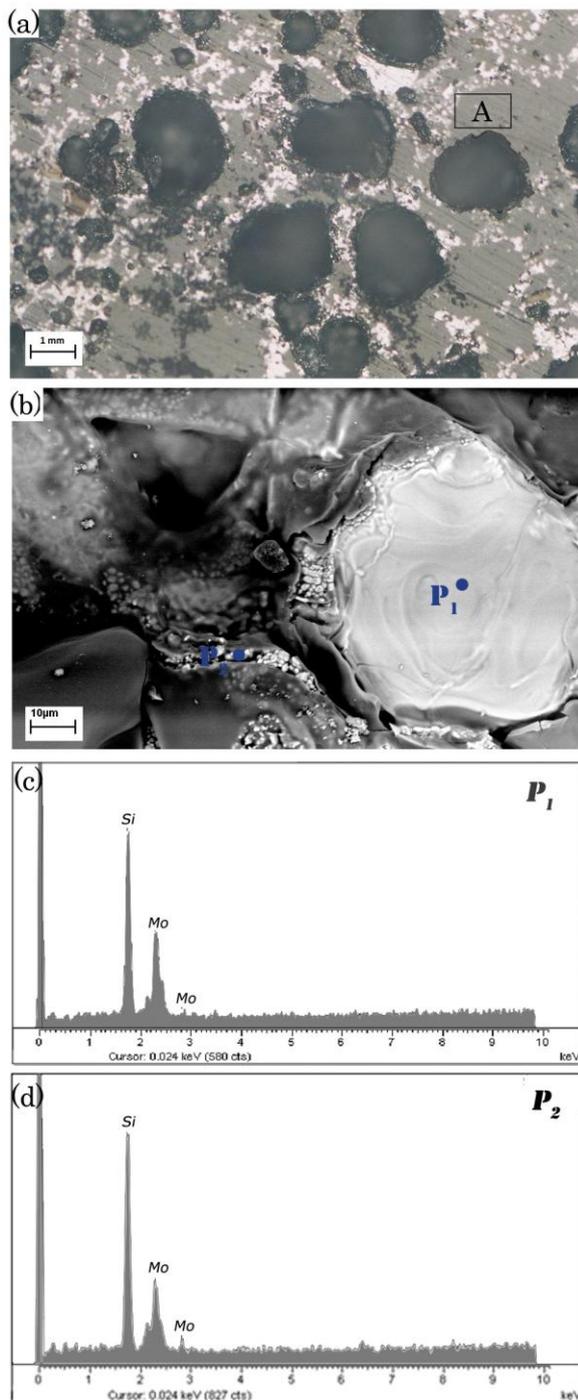
Fig. 5. a) Metallographic images of samples synthesized with Y=2.5. The SEM and EDX elemental map of the area denoted "A" is shown in Fig. 5b,c,d. b) The Secondary electron SEM micrograph of the combustion synthesized specimen (Y=2.5). c,d) The EDX spectra of points P1 and P2 in Fig. 5b.

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The low fluidity of the produced and the lack of enough time for the produced CO gas to move in the matrix caused the pores to appear with a closed morphology.

Increasing the blending ratio to Y=2.5 increased the amount of produced CO gas and also caused the theoretical adiabatic temperature to reduce to 1530 0C, and as the propagation rate of the reaction was not

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