

## The rapid synthesis of MoSi<sub>2</sub> for high-temperature furnace heating elements

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### Abstract

The combustion characteristics of the disilicides molybdenum system have been studied experimentally. The pertinent reaction parameters that control self-propagating high temperature synthesis reactions have been examined. These include reactant particle size, powder mixing and compaction, reaction stoichiometry, diluents. The influence of experimental variables on integrity, uniformity, structure, and related material properties will be discussed. Formation mechanism of MoSi<sub>2</sub> during SHS might be different and depending on experimental conditions.

**Key words** : Combustion synthesis, SHS, combustion velocity, combustion temperature, MoSi<sub>2</sub>.

### 1. INTRODUCTION

Ceramics for heating elements, including MoSi<sub>2</sub>, produced by conventional methods, such as sintering and hot-pressing, require expensive high-temperature process steps and machining, which add significant cost to the material [1,2]. The use of exothermic, self-propagating reactions (SHS), has been of interest for forming high-purity refractory compounds. SHS defined, as material synthesis by combustion is therefore an interdisciplinary research subject in the material science. The underlying basis of SHS relies on the ability of highly exothermic reactions to be self-sustaining and, therefore, energetically efficient [3]. The cost-effective production of hard, strong, and dense refractory materials has been claimed. The silicides of molybdenum used for manufacturing various constructional ceramics and high-temperature heaters owing to its excellent oxidation resistance, reasonable strength, good thermal- and electroconductivity at high-temperatures. Such materials are usually obtained by heat

treatment at 1300-1500 °C in hydrogen medium.

In this paper we attempt to clarify the reaction mechanism in the MoSi<sub>2</sub> synthesis produced by reducing of molybdenum oxide by Al as active metal and its reaction with Si. We investigated the influence of the sample diameter, preheating, particle size on the formation of a homogeneous product and in situ stability of the molybdenum-silicon system properties.

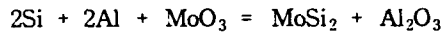
### 2. EXPERIMENTAL PART

All reagent powders of different particle sizes (MoO<sub>3</sub>, Si, and Al) were obtained from Aldrich (U.K.) and used as supplied. Milling operations were carried out in a FRITSCH ball mill (Germany). The mixture was pressed (20 kg/cm<sup>2</sup>) into cylindrical pellet. The pellet was supported on a ceramic boat and the reaction ignited by an electrically heated nichrome wire filament at one end. This produces a solid flame that moves out from point of initiation through the whole material. In our experiment redox process with large heat release has been made according the scheme:

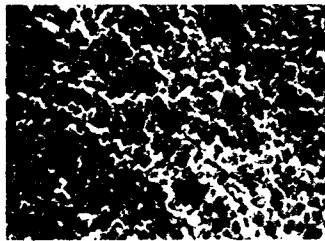
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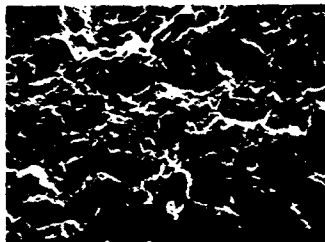
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Argon was admitted through the tube (10 l/min). It was observed a bright-yellow propagation wave that proceeds through the solid at the velocity 3-4 mm/s and combustion temperature 1700-1800 °C. Reactants when mixed in stoichiometric proportions after reaction always produced main tetragonal phase molybdenum disilicide with the standard peaks from JCPDS card # 6-681. A non-electroconductive component is represented by 10-15 % of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The uniformity of the dispersion was verified by scanning electron microscope (SEM) micrographs. The dilution of the reactants mixture was achieved by using an excess of silicon or molybdenum disilicide. The phase composition remained unchanged, even when the reactants mixture was diluted by excess silicon or molybdenum disilicide. The micrograph in Fig.1a shows the product particles that were obtained by SHS appear to be largely spherical and porous.



(a)



(b)

Fig.1. Micrographs of fracture surface of the MoSi<sub>2</sub> sample after SHS process (a) - for powder synthesis); and (b) - as electric heater element (densificated sample-sintering article).

Synthesis and densification for ceramics can be achieved simultaneously by combining the SHS and high-pressure techniques. The first experiment was conducted by igniting the mixed powders (Fig.1a). During the second experiment we used Miyamoto-method [4] of gas-pressure combustion sintering (Fig.1b). In this method the reactants is vacuum-sealed into a glass capsule. Just as in the capsule method for HIPing, and embedded into a combustion agent, such as the mixed powders of Si and C. The reaction is initiated by the high heat release from the combustion agent, which is ignited at the glass softening temperature under Ar-gas pressures below 100 MPa. Nearly fully dense MoSi<sub>2</sub>, SiC and their composites have been fabricated by this process [4.]

### 3. RESULTS AND DISCUSSION

The analysis of solid-solid combustion reaction in the SHS regime is quite difficult, mainly because of the complex interaction between solid reactants. SHS propagation velocities can be controlled by a number of methods. The addition of diluents, usually in the form of the powdered product, has been used to decrease propagation velocities through a reduction in the heat energy liberated per unit mass of precursor powder. In our experiments release energy was 1061 kJ/mol, and adiabatic temperature exceeds 3000 °C. Diluents technique leads to reduce post synthesis sample temperatures, which can make the compaction more difficult. Propagation velocities have also been varied through control of the size of the precursor powder particles with the larger particle sizes yielding lower velocities.

#### a) Effects of mixture ratio,

Mixture ratio  $\mu$  is one of the controllable parameters in preparing a test specimen and is commonly used in experiments to specify the nature of the initial compact. The range of flammability expands with increasing initial temperature  $T_0$ , heat reaction  $q$ , and metal concentration, but contrasts with increasing

melting point  $T_m$ . Figure 2 shows the combustion velocity  $v_c$  for the Mo-Si system as a function of stoichiometry, with initial temperature  $T_0$  taken as a parameter.

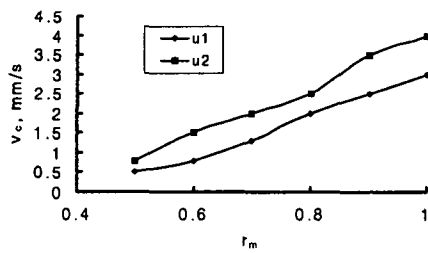


Fig.2. Combustion velocity for Mo-Si system as a function of the mixture ratio  $r_m$ , with the initial temperature  $T_0$  (1 curve at 673 K; 2 curve at 973 K) taken as a parameter and the Si particle radius  $R_0 = 3-5 \mu\text{m}$ .

b) Effects of initial temperature,  $T_0$

Initial temperature  $T_0$  is also one of the controllable parameters in experimentation, and its effects on the combustion velocity have been examined extensively. Fig.3 shows  $u_0$  for the Mo-Si system as a function of  $T_0$  for  $r_m = 1.0$ . The Si particle radius is set to  $R_0 = 3-5 \mu\text{m}$  in accordance with experimental data. The trend of increasing  $u_0$  with increasing  $T_0$  is due to the preheating effect, as expected.

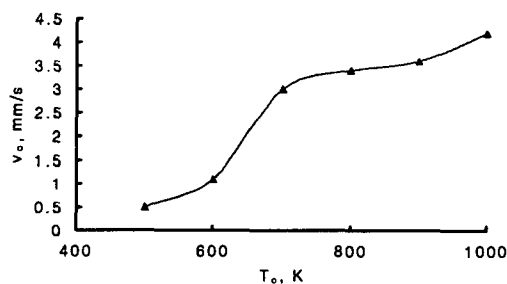


Fig.3. Combustion velocity for Mo-Si system as a function of the initial temperature  $T_0$ , the mixture ratio  $r_m = 1$ , and the particle radius  $R_0 = 3-5 \mu\text{m}$ .

As for the deviation at high temperature, there is the possibility that it is caused by the experimental

determination of  $T_0$ . That is, the real  $T_0$ , before arrival of the flame front, could be higher than the ambient temperature, because of the heat associated with the ignition source.

c) Effects of particle radius,  $R_0$

Since SHS reactions are normally conducted using a powder compact, e. g. pellets made from powders, the particle packing characteristics play an important role in controlling the green density, green pore size, thermal conductivity of reactants and products, and inevitably affect the consolidation and properties of the final products. Particle radius,  $R_0$  is the important parameter, which specifies the heterogeneity in the reaction zone. The other dependence in Fig. 4. shows the decrease in the combustion velocity with the increase in the size of Si particles. It is of interest that the combustion velocity  $v_c$  is practically constant down to  $100 \mu\text{m}$ .

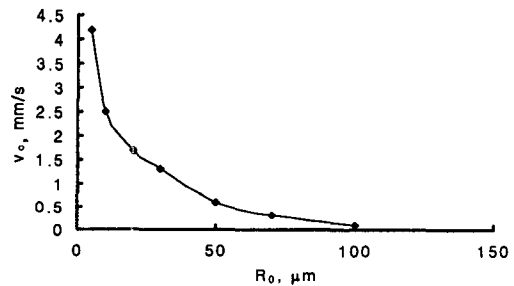


Fig.4. Combustion velocity as a function of the initial particle of Si radius  $R_0$ ; stoichiometric mixture ( $\mu_0=1.0$ ),  $T_0 =973 \text{ K}$ .

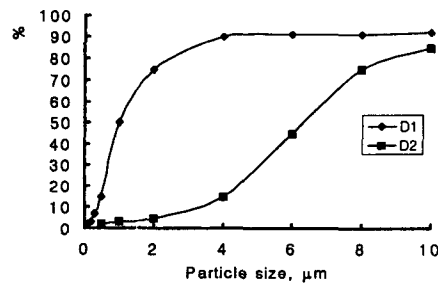


Fig.5. Effect of particle size distribution on the green density of the compact (D1=65%; D2=55%)

Frequently, mono sized spheres are used as

models for characterizing the patterns of particle packing. Varying the particle size can control the combustion velocity. In our experiments all initial compounds were highly variable in character and exhibit considerable distributions in size, shape and agglomeration. In this case particles were mostly packed in non-ordered arrangements and the random packing density of uniform spheres is reported to vary from 55 to 65 %. The distribution of particle size significantly affects the packing density,  $D$  (Fig.5).

When smaller particles are introduced and distributed in the interstices of larger particles, the packing density increases and the porosity and pore size decrease substantially. The particle shape and surface roughness can also affect the inter particle friction, bringing of the particles and hence the packing density. The packing density will decrease as the shape departs from equiaxed (spherical) for similarly sized powders. Similarly, the green density improves as the roughness of particle surface decreases. The use of vibration helps us to attain a high packing density, but suddenly we meet problems with agglomeration and size segregation.

#### 4. CONCLUSION

In the present investigation, the study shows that combustion propagation in SHS is indeed a heterogeneous process, that combustion is diffusion-limited for the systems examined, and that the range of flammability as well as effects of stoichiometry, initial temperature, and particle size on the flame propagation rate. The compaction of green powders is not only influenced by particle size and shape, but also strongly affected by powder handling and consolidation. As mentioned earlier, the final product morphologies and properties are dependent on the particle size and shape, similarly, the compaction of green powders also plays an important role in the combustion synthesis reaction. The complete mixing of reactants powders is essential for the completion of a reaction and to produce uniformity in the product structure. The structural imperfections of the materials produced through the SHS reaction (micro-porosity, lamination, cracking) is very useful

for powder synthesis, but not for SHS sintering of solid products for the manufacture of articles of desired form and size. This is one of the promising technologies. Conventional methods of sintering ceramic articles (hot pressing, gasostat hot pressing) are characterized with high capital and energy consumption. The production of ceramic materials and articles in the direct synthesis of a metal/non-metal-gas system in the combustion regime without a preliminary stage of ceramic powder preparation and subsequent densification up to required form and size is of great interest. Changing the combustion conditions, namely, its physico-chemical and technological parameters, can solve the problem of the product structure control.

#### ACKNOWLEDGEMENT

This work was accomplished by KISTEP grant of M1-0011-00-0043 for Intl. joint-research program and '00RU03-19-001 for exchange scientist program.

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