Mechanically activated combustion synthesis of molybdenum borosilicides for ultrahigh-temperature structural applications

CrossMark

Alan A. Esparza, Evgeny Shafirovich[*]

Department of Mechanical Engineering, The University of Texas at El Paso, El Paso, TX 79968, USA

A B S T R A C T

The thermal efficiency of gas-turbine power plants could be dramatically increased by the development of new structural materials based on molybdenum silicides and borosilicides, which can operate at temperatures higher than 1300 °C with no need for cooling. A major challenge, however, is to simultaneously achieve high oxidation resistance and acceptable mechanical properties at high temperatures. Materials based on Mo_5SiB_2 (called T_2) phase are promising materials that offer favorable combinations of high temperature mechanical properties and oxidation resistance. In the present paper, T_2 phase based materials have been obtained using mechanically activated self-propagating high-temperature synthesis (MASHS). Upon ignition, Mo/Si/B/Ti mixtures exhibited a self-sustained propagation of a spinning combustion wave, but the products were porous, contained undesired secondary phases, and had low oxidation resistance. The "chemical oven" technique has been successfully employed to fabricate denser and stronger Mo_5SiB_2—TiC, Mo_5SiB_2—TiB_2, and Mo—Mo_5SiB_2—Mo_3Si materials. Among them, Mo_5SiB_2—TiB_2 material exhibits the best oxidation resistance at temperatures up to 1500 °C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The thermal efficiency of gas-turbine power plants could be increased by the development of new structural materials based on molybdenum silicides and borosilicides, which can operate at temperatures higher than 1300 °C with no need for cooling [1—4]. Molybdenum disilicide ($MoSi_2$) has a high melting point (2030 °C) and excellent high-temperature oxidation resistance, but a single $MoSi_2$ phase has low fracture toughness at room temperature and low strength at elevated temperatures [5]. The mechanical properties of Mo-richer silicides such as Mo_5Si_3 (called T_1) phase and Mo_3Si are better, but they have lower oxidation resistance [4,5].

A promising approach focuses on adding boron to Mo-rich silicides [6]. The addition of boron improves oxidation resistance because of the formation of a borosilicate surface layer [1,6]. This has promoted interest in fabricating Mo_5SiB_2 (called T_2) phase.

Boron addition, however, makes silicides brittle. One way to toughen these mixtures is to add molybdenum phase. Three-phase α-Mo—Mo_5SiB_2—Mo_3Si (e.g., Mo—12Si—8.5B) alloys are considered as promising materials that combine good oxidation resistance and

acceptable mechanical properties [7—9].

A novel method for improving the mechanical properties of Mo_5SiB_2 materials involves the addition of titanium carbide (TiC), which has a melting point of 3160 K and a modulus of elasticity of 379 GPa at 1000 °C [10]. Recently, it has been shown that the addition of TiC improves the compression strength of Mo—Si—B materials at high temperatures [11,12].

One more potential additive to T_2 phase is titanium diboride (TiB_2). The melting point of TiB_2 is 3230 °C and its elastic modulus is 534 GPa at 1000 °C [13], i.e. these properties of TiB_2 are even better than those of TiC. However, to the best of our knowledge, the phase diagram for TiB_2 and Mo—Si—B phases is not available and no attempt has been made to fabricate Mo_5SiB_2—TiB_2 materials.

The synthesis of Mo—Si—B multi-phase alloys is usually difficult because of their extremely high melting temperatures. Mechanical alloying has been considered as a promising method for manufacturing these materials [9,14,15]. This method, however, requires relatively long milling times (typically 10—100 h), leading to large energy consumption and contamination of the product by grinding media [9].

It would be attractive to use self-propagating high-temperature synthesis (SHS) for the fabrication of T_2 phase based alloys. A major problem, however, is low exothermicities of mixtures for producing these materials. One promising method for enabling the SHS

* Corresponding author.
E-mail address: eshafirovich2@utep.edu (E. Shafirovich).

process in low-exothermic mixtures is mechanical activation of the powders, i.e., a short-duration, high-energy ball milling step before the combustion process [16,17]. The entire procedure is usually called mechanical activation-assisted (or mechanically activated) self-propagating high-temperature synthesis (MASHS). The high-energy milling enables intermixing of reactive components on a very small scale. The fracture-welding process during milling increases the contact surface area and destroys the oxide layer on the particle surface. As a result, mechanical activation improves the reaction kinetics, leading to an easier ignition and stable combustion. Also, the short milling time eliminates the problem of product contamination by milling media, typical for mechanical alloying. In general, the MASHS technique combines the advantages of mechanical alloying and SHS, also allowing for the formation of materials that cannot be obtained by either of these techniques if used alone.

Sometimes, however, the use of mechanical activation is insufficient for ignition. In such cases, the exothermicity can be increased by changing the mixture ratio. For example, in the prior research [18], mixtures with Mo/Si/B mole ratio of 5:1:2 (which corresponds to T_2 phase) did not burn, while changing the composition toward two products, *viz.* T_2 phase and MoB, resulted in a self-sustained combustion. Note that in these experiments, a spinning combustion wave was observed, with the motion of hot spots along a helix on the pellet surface. This regime, called spin combustion, occurs in some low-exothermic mixtures when the released heat is not sufficient for maintaining a planar combustion front [19–22].

Based on results [18], one may expect that promising Mo_5SiB_2/TiC and Mo_5SiB_2/TiB$_2$ materials can be fabricated by MASHS of Mo/Si/B mixtures with added Ti/C or Ti/B mixtures because the reactions of Ti with C and B are highly exothermic (the formation enthalpies of TiC and TiB$_2$ are −184.10 kJ/mol and −279.49 kJ/mol, respectively [23], and the adiabatic flame temperatures of stoichiometric Ti/C and Ti/2B mixtures, calculated at 1 atm pressure with THERMO software [24], are 3290 K and 3193 K, respectively).

Another method for burning low-exothermic mixtures is the so-called "chemical oven," where the sample is surrounded by a layer of a highly exothermic mixture such as Ti/C or Ti/B. Combustion of this layer releases enough heat for enabling ignition and combustion of the core material. Recently, this method has been successfully employed for the fabrication of T_2 phase [25].

The objective of the present work was to investigate the feasibility of using MASHS for the fabrication of promising materials based on Mo_5SiB_2 phase such as α-Mo/Mo_5SiB_2/Mo_3Si, Mo_5SiB_2/TiC, and Mo_5SiB_2/TiB$_2$ materials. First, the attempts were made to synthesize the materials with TiC and TiB$_2$ phases using SHS in Mo/Si/B mixtures with added Ti/C and Ti/B. Next, the chemical oven technique was used to fabricate these materials and α-Mo–Mo_5SiB_2–Mo_3Si alloys as well. Characterization of the obtained materials included X-ray diffraction analysis, determination of mechanical properties, and oxidation studies involving thermoanalytical methods.

2. Experimental

Molybdenum (99.95% pure, Climax Molybdenum), silicon (crystalline, 99.5% pure, Alfa Aesar), boron (amorphous, 94–96% pure, Alfa Aesar), graphite (crystalline, 99% pure, Alfa Aesar), and titanium (99.5% pure, Alfa Aesar) powders were used in this study.

The powders were mixed in a three-dimensional inversion kinematics tumbler mixer (Inversina 2L, from Bioengineering, Inc.) for 1 h and then milled in a planetary ball mill (Fritsch Pulverisette 7 premium line). Zirconia-coated 80-mL bowls were used. The grinding media were 1.5-mm zirconia balls. The mixture to ball

mass ratio was equal to 1:6. The milling process was conducted in an argon environment. It included 4 milling–cooling cycles (10 min milling at the maximum rotation speed of 1100 rpm and 75 min cooling). As reported previously [18], after this milling regime, the particle size of Mo/Si or Mo/Si/B mixtures decreases from about 10 μm to the submicron range (200–500 nm), while X-ray diffraction analysis detects only initial reactants with no products.

To fabricate Mo_5SiB_2–TiC materials by conventional SHS (with no external heat), four compositions were tested. Different amounts (10 wt%, 20 wt%, 30 wt%, and 40%) of stoichiometric Ti/C (1:1 mol ratio) mixture were added to the main Mo/Si/B (5:1:2 mol ratio) mixture. To fabricate Mo_5SiB_2–TiB$_2$ materials by the same technique, five compositions were tested. Different amounts (10 wt %, 15 wt%, 20 wt%, 30 wt%, and 40 wt%) of stoichiometric Ti–B (1:2 mol ratio) mixture were added to Mo/Si/B (5:1:2 mol ratio) mixture. The resulting mixtures were compressed into cylindrical pellets (diameter 13 mm) in a uniaxial hydraulic press (Carver) with a compressive force of 35–40 kN. Before compacting, a layer of Ti/B (1:2 mol ratio) booster mixture was placed on the top of the pellet. The height of the main mixture was 12–15 mm and the height of the booster layer was about 3 mm. The relative densities of the tested mixtures were in the range of 57–66%.

In the chemical oven technique, composite pellets were prepared that included a core made of the main mixture and a shell made of the Ti/B booster mixture. The core compositions for fabricating Mo_5SiB_2–TiC and Mo_5SiB_2–TiB$_2$ materials consisted of 85 wt% Mo/Si/B (5:1:2 mol ratio) mixture and 15 wt% Ti/B (1:2 mol ratio) or Ti/C (1:1 mol ratio) mixture. The core compositions for fabricating α-Mo–Mo_5SiB_2–Mo_3Si materials consisted of Mo, Si, and B mixed according to the composition of Mo–12Si–8.5B alloy. To make the composite pellet, first, the core mixture was compacted into a pellet (diameter: 13 mm, height: 12.8–14.0 mm) using a force of 35–40 kN. Then this pellet was submerged into Ti/B mixture inside a 25-mm die and pressed again. The resulting composite pellet had a height of 23–26 mm. This pellet was wrapped by 3-mm-thick thermal paper (Fiberfrax). Fig. 1 shows sketches of pellets prepared for conventional SHS and chemical oven experiments.

The combustion experiments were conducted in a 30-L stainless steel reaction chamber. A schematic diagram of the setup is shown elsewhere [26]. The pellet was installed vertically on a ceramic fiber insulator (Fiberfrax). The chamber was evacuated and filled with ultrahigh purity argon at 1 atm. The pellet was heated by a tungsten wire connected to a DC power supply. During conventional SHS, propagation of the combustion front over the pellet was observed, while in the chemical oven experiments, it was possible to only see bright light emitted by the burning shell. In both types of experiments, the power supply was shut off upon the ignition of the booster mixture.

WRe5%/WRe26% thermocouples (type C, wire diameter: 76 μm, Omega Engineering) were used to measure the temperature in the middle of the sample during the combustion process. The thermocouples, located in two-channel ceramic insulators, were
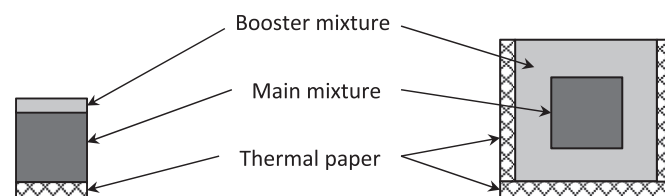

Fig. 1. Sketches of pellets prepared for conventional SHS (left) and chemical oven experiments (right).