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Mechanically activated combustion synthesis and shockwave consolidation of magnesium silicide

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ABSTRACT

Magnesium silicide (Mg_2Si) is a promising intermetallic compound for applications such as light-weight composite materials and thermoelectric energy conversion. It is difficult, however, to synthesize high-quality Mg_2Si on a large scale. Self-propagating high-temperature synthesis (SHS) is an attractive pathway, but it is difficult to ignite the low-exothermic Mg/Si mixture and achieve a self-sustained propagation of the combustion wave. In the present paper, mechanical activation was used to facilitate the ignition. Magnesium and silicon powders were mixed and then milled in a planetary ball mill in an argon environment. The mixtures were compacted into pellets and ignited at the top in a reaction chamber filled with argon. Depending on the pellet dimensions and diameter-to-height ratio, two modes of combustion synthesis, *viz.*, thermal explosion and SHS, were observed. In both modes, Mg_2Si product was obtained. Thermocouple measurements have revealed that the exothermic reaction stages include two self-heating events separated by a long period of relatively slow interaction. To clarify the reaction mechanisms, differential scanning calorimetry was used, which also revealed two peaks of exothermic reaction in the milled Mg/Si mixture. The first peak is explained by the effect of mechanical activation. Explosive-based shockwave consolidation was used to increase the product density. Thermophysical properties of the obtained material were determined using a laser flash apparatus.

1. Introduction

Magnesium silicide (Mg_2Si) is a promising intermetallic compound for various applications. Owing to its low density (1.99 g/cm^3), high melting point (1102 °C), and excellent mechanical properties, Mg_2Si is used as a reinforced phase in composite materials for automotive, aerospace, and other industries [1]. In recent years, Mg_2Si has attracted attention as an attractive material for thermoelectric energy conversion at temperatures ranging from 200 °C to 500 °C [2–5], i.e., in the operation domain of devices for energy harvesting. An important advantage of Mg_2Si-based thermoelectric materials is that magnesium and silicon are non-toxic, abundant, and relatively inexpensive constituents [3].

Magnesium silicide can be synthesized on a small scale via melting and solidification [2]. However, the large difference between the melting points of Mg (650 °C) and Si (1414 °C) leads to inhomogeneous microstructure with coarse grains [6]. Also, scaling up these methods is problematic since the high vapor pressure of Mg results in the loss of Mg and poor control over stoichiometry [7].

Mechanical alloying has been considered, but this method requires long milling times, leading to contamination by materials of the milling media [6–10]. The recently proposed incremental milling technique still requires several hours of milling [7].

Magnesium silicide materials have also been obtained by solid-state reaction synthesis. Specifically, Mg and Si powders with or without dopants were mixed, cold-pressed to pellets, wrapped with foil or placed in crucibles, sealed in quartz tubes under vacuum, and heated at 400–600 °C for 1–2 h [11–13] or as long as 3.5 days [14]. Microwave sintering has also been used [15]. These methods involve external heat and large energy consumption.

A negative formation enthalpy (−77.82 kJ/mol) of Mg_2Si, however, implies that it can be produced by combustion synthesis, which is recognized as a cost-effective, efficient, and clean method for the production of advanced materials [16–22]. A major advantage of combustion synthesis is low energy consumption – the process is sustained by the heat of the exothermic reaction between constituent powders. Other advantages of combustion

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synthesis include simple and inexpensive equipment, short processing time, tailored microstructures and properties, and higher purity of the products [16–22].

Combustion synthesis in the mixture of powders may occur in two modes. One is thermal explosion, sometimes called volume combustion synthesis. In this mode, the entire sample is heated uniformly (e.g., in a small furnace or a heated crucible) until the reaction occurs essentially simultaneously throughout the volume. This mode of combustion synthesis is often used for weakly exothermic reactions that require preheating prior to ignition [20]. The second mode is self-propagating high-temperature synthesis (SHS), where a sample is ignited locally at one end, leading to a self-sustained travel of the combustion wave over the sample.

Thermodynamic calculations with THERMO software [23] show that the adiabatic flame temperature for the mixture of 2 mol Mg and 1 mol Si at 1 atm is only 1242 K (969 °C). At such low values of the adiabatic flame temperature, it is usually difficult to achieve a self-sustained combustion without preheating. Thus, it is not surprising that combustion synthesis of magnesium silicide from elemental magnesium and silicon has been conducted first in the thermal explosion mode. Specifically, a pellet of compacted Mg/Si mixture was installed vertically between two rams, heating of which led to the thermal explosion and formation of Mg_2Si [24].

More recently, Mg_2Si has been synthesized from elemental Mg and Si by placing a Mg/Si mixture in a resistance-heated ceramic crucible [25,26]. The researchers used the unusual term “global ignition,” but it is clear that the reaction was occurring in the thermal explosion mode.

Although Mg_2Si was successfully obtained in thermal explosion experiments [24–26], it is attractive to fabricate it in the SHS mode (a pellet ignited at one end and the combustion wave propagates over the pellet), which makes it feasible to control the process and the product composition, consumes less energy, and can be scaled-up easier. Note that industrial reactors for combustion synthesis in the SHS mode have been developed and commercialized [21].

One promising method for enabling the SHS 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 [27–32]. 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 between reactants and destroys the oxide films on their surfaces. As a result, mechanical activation improves the reaction kinetics, leading to an easier ignition and stable combustion. Further, the short milling time eliminates the problem of product contamination by milling media, typical for mechanical alloying.

To yield a useful structural or functional material, products obtained by methods of powder metallurgy (mechanical alloying, solid state synthesis, etc.) must be densified. This is fully related to combustion synthesis, which usually produces porous products. There are a number of approaches for achieving densification, all involving a combination of heat and pressure. For example, in hot pressing, a powder is pressurized at a relatively high temperature for a significant time to allow interparticle bonding, void closure, and densification. Unfortunately, the long duration of hot pressing allows significant grain growth, causing deterioration of thermoelectric and other properties.

If the material to be densified is conductive, spark plasma sintering (SPS) may be used where powder is compacted in a uniaxial die and electrical current is passed through the material. Self-heating at powder contact points causes adjacent particles to bond, leading to void closures and densification. SPS has been used to densify Mg_2Si powders obtained by solid-state reaction synthesis in furnaces [11] and microwave ovens [33] or by melting and grinding [34]. Moreover, SPS was used to produce dense Mg_2Si materials from Mg and Si or from MgH_2 and Si in one step, where the reaction occurred during the SPS process [33,35–38]. A similar method, called field-activated and pressure-assisted reactive sintering (FAPAS) has also been used for the same purpose [39]. The relatively short process time in SPS and FAPAS methods mitigates the grain growth and improves thermoelectric properties.

There exists, however, an even faster method, shockwave consolidation, where also attainable pressures are much higher. During shockwave consolidation, densification and interparticle bonding occur so quickly that grain growth can be totally suppressed and the material retains its nano- or amorphous structure [40].

The objectives of the present paper are to explore the feasibility of using mechanical activation for enabling a self-sustained propagation of the combustion front over Mg/Si mixture pellets and to demonstrate shockwave consolidation of Mg_2Si products.

2. Experimental

Magnesium (−325 mesh, 99.8% pure, Sigma-Aldrich) and silicon (crystalline, −325 mesh, 99.5% pure, Alpha Aesar) powders were mixed in the stoichiometric proportion (Mg/Si mole ratio: 2) in a three-dimensional inversion kinematics tumbler mixer (Bioengineering Inversina 2L) for 1 h. Next, the mixtures were milled in a planetary ball mill (Fritsch Pulverisette 7 Premium Line) using zirconia-coated grinding bowls and zirconia grinding balls (diameter: 3 mm, the balls-mixture mass ratio: 5:1). The milling was conducted in an argon environment at 750 rpm for 20 min. To decrease temperatures and prevent reactions during milling, the process was separated to cycles with 75-min cooling pauses between milling periods.

The mechanically activated Mg/Si mixtures were cold-pressed into cylindrical pellets using a uniaxial hydraulic press (Carver). Two pellet sizes were used. The smaller pellets, compacted at a force of 19.6 kN, had a mass of 3.3–4.0 g, a diameter of 13 mm, and a height of 17–21 mm. The larger pellets, compacted at 29.4 kN, had a mass of 8 g, a diameter of 25 mm, and a height of 17 mm.

The combustion experiments were conducted inside a windowed stainless steel chamber (diameter 30 cm, height 40 cm), connected to a compressed argon cylinder and a vacuum pump. A schematic diagram of the setup is shown elsewhere [41]. The pellet was placed on a metal pedestal, insulated with ceramic fiber paper (Fiberfrax), inside the chamber, which was then three times evacuated and filled with ultra-high purity (99.999%) argon at 1 atm pressure. The pellet was ignited at the top with a tungsten coil, heated by a DC power supply. After ignition, the DC power supply was turned off. Propagation of the combustion wave was recorded with a high-resolution video camera (Sony XCD-SX90CR). In some of the experiments with 25-mm-diameter pellets, the temperature in the center of the pellet was measured with a thermocouple (254-μm diameter wire, K-type, Omega Engineering) at a sample rate of 100 Hz. The thermocouple, located in a two-channel ceramic insulator, was inserted into the pellet through a channel drilled perpendicularly to the pellet axis and connected to a USB-based data acquisition system (National Instruments USB-9211).

Compositions of the milled powders and combustion products were studied using X-ray diffraction analysis (Bruker D8 Discover XRD). Particle size distributions in these powders were studied with a laser diffraction particle size analyzer (Microtrac Bluewave).

To understand the reaction mechanisms and explain the time variation of temperature obtained in the combustion experiments, thermal analysis of milled Mg/Si mixtures was conducted using a