

Reaction Sintering of Mg_2Si Thermoelectric Materials by Microwave Irradiation

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ABSTRACT: In order to reduce the oxidizing and volatilizing caused by Mg element in the traditional methods for synthesizing Mg_2Si compounds, solid state phase reaction at low temperature was introduced by microwave field. XRD was used to characterize the powders. At the same time, the influences of parameters during the synthesis processing were discussed. The results suggest that the heating profile is also dependent on the initial green density and higher green density

1. Introduction

Magnesium silicide (Mg_2Si), having a face-centered-cubic CaF_2 type of structure, has been identified for a promising advanced thermoelectric materials in the temperature range from 500K to 800 K[1~4], because of their advantages of an environmental-friendly material, such as the abundance of its constituent elements in the earth's crust and the non-toxicity of its processing by-products[5,6]. However, the phase purity and microstructure of the product Mg_2Si are difficult to control by conventional melting processes such as ingot metallurgy (IM) because of the easy volatilization and oxidation of Mg and the great discrepancy of melting point between Mg and Si. Here to fore, many preparation methods have been developed to produce Mg_2Si and improve its thermoelectric properties, such as vacuum melting[4], solid state reaction[7], mechanical alloying[8-10] and spark plasma sintering (SPS)[3,11], which are quite time consuming and complex. However, the above issues have not solved radically yet.

These problems mentioned above motivated the development of a new synthetic method that overcomes these problems and facilitates product formation. The microwave-assisted synthesis method is presented. This method is a very promising preparation method for many materials because it is fast, clean, energy efficient and does not suffer from the disadvantages of the classical preparation technique. Many materials have been synthesized by the microwave method at considerably lower temperature and in shorter time than the conventional methods[12,13]. Until recently, microwave processing was mostly restricted to ceramics, cemented carbides and ferrites[14]. Applicability of microwave sintering to

provides lower heating rate while power setting are fixed and the oxidation of Mg can be restrained by changing microwave heating programs. It was found that high purity Mg_2Si intermetallic compound can be obtained with excessive content of 8at% Mg from the stoichiometric Mg_2Si , 853K and 30min.

Keywords: Mg_2Si ; thermoelectric materials, solid state reaction method, microwave synthesis

metals was ignored due to the fact that they reflect microwaves. Roy et al.[12] reported that particulate metals can be heated rapidly in microwaves. This has led to the use of microwaves to consolidate a range of particulate metals and alloys[15].

In this paper, Mg_2Si thermoelectric materials were prepared by microwave-assisted activation synthesis, which has not been reported before. It is a rapid process and results in a purity phase material. The results obtained seem to be very interesting and stimulate further research in this direction.

2. Experimental Procedure

Figure.1 shows a schematic illustration of the experimental equipment, which was used for the production of activated Mg and Si particles. It mainly consists of a microwave oven and a heat preservation system.

Due to the volatility of Mg during the synthesis of this compound, the excessive content of Mg is indispensable. In this study, samples with nominal formula $Mg_{2.08}Si$ were prepared. The samples were prepared as follows: according to the stoichiometric proportion of Mg_2Si , 2.08:1 atomic ratio of Mg (>99.5mass% purity, 200mesh) and Si (>99.5mass% purity, 300mesh) were mixed by an ultrasonic homogenizer in ethanol for 45min. After being completely dried in the cabinet, they were compressed to form pellet 10mm in thickness and 20mm in diameter under appropriate pressure. The samples were then placed in alumina crucible in the center of the microwave oven and the solid-state reaction was carried out under the protection of high purity Ar (99.9%). The microwave

oven used in the present work consists of a 2.45GHz microwave generator with continuous adjustable power output 0–15kW. An infrared pyrometer was used (Raytek, Marathon series) for temperature measurement. Microwave heating used in the present work was carried out at the power level of 2.0kW–3.5kW and heated to a designed temperature (580°C–600°C) and kept at this temperature for 20–40min. The samples were cooled to room temperature for further control experiment raw materials. Phases of the fabricated materials were detected by X-ray diffraction (D/Max-III A) with Cu K α radiation ($\lambda=0.15406$ nm).

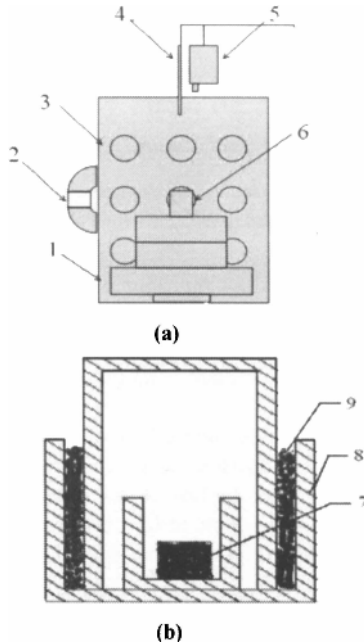


Figure 1. Schematic view of microwave system setup (a) and Schematic view of the crucible (b)

1—rotating table; 2—peep hole; 3—magnetron tube; 4—infrared thermometer; 5—thermocouple; 6—crucible; 7—Mg, Si samples; 8—alumina; 9—Mg powder

3. Results and Discussion

3.1 Heating Behavior of the Mg and Si fixed power compacts

Figure 2. shows the experimental temperature rise with time in Mg and Si fixed power compacts with 40%, 50% and 60% theoretical density, respectively, for a specific particle size while keeping constant the power setting and total exposure time. It is interesting to note that the porous metal compacts couple with microwaves and get heated up rapidly and the heating rate increases as the green density decreases (porosity increases). Higher is the porosity, higher is the heating rate. The temperature rise is restricted to a certain level.

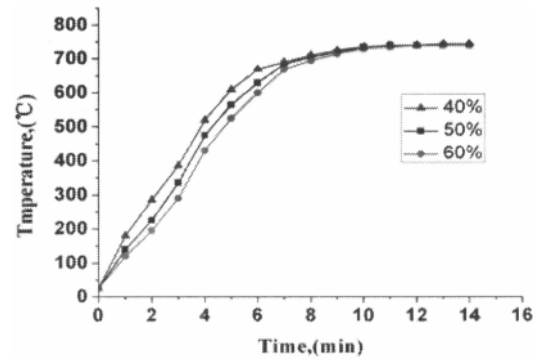


Figure 2. Comparison of temperature-rising rate of Mg and Si compacts as a function of initial porosity in microwave furnace.

It is well known that an incident wave on a conductive metallic material is mainly reflected, and microwaves for electrically conducting materials do not penetrate a bulk sample beyond the skin depth. The skin depth “ δ ” (m) is defined as the depth into the conductor from the surface at which the current density is 1/e of its value at the surface, given by the well-known expression (1)[16]

$$\delta = \sqrt{\frac{2}{\omega \sigma \mu}} \quad (1)$$

Here, μ is the real part of the permeability taken to be 4×10^{-7} T m/A for nonmagnetic materials. σ and ω are the DC electrical conductivity and angular frequency, respectively. At 2.45 GHz, the skin depth of bulk magnesium is about $2.18 \mu\text{m}$. But as in case of porous material electrical conductivity decreases with an increase in porosity so from the above equation effective skin depth should also increase. Johnson and co-workers[15] measured the values of σ the conductivity of green copper powder. These measurement results show the sample conductivity is far below that of bulk copper. However, the initial skin depth of porous copper powder metal compacts is much larger—on the order of 0.05m (computed using Eq.(1) and the measured values of σ). For a lossy conductor, the electric currents may not be zero so the electric field E is not zero because of finite conductivity according to Ohm’s law $J=\sigma E$. which shows that at microwave frequencies the magnetic induction is much larger than the electric field, so the microwave heating of powdered metals mainly as the result of magnetic induction heating. Roy, et[11] al also attributed the heating of metals to eddy-current losses from the electric field. Thus an induction loss caused by eddy currents is one mechanism for microwave sintering of Mg_2Si compound. A similar phenomenon was also found by Booske, et al[16].

3.2 Effect of the power of microwave on

Mg₂Si compounds

In order to find out the complete reaction temperature of Mg, Si to form Mg₂Si in microwave chamber, the raw mixed powder were sintered by microwave at temperatures from 573 K to 903 K. When the input power was kept constant at 2.5kw and temperature is at 853K, Mg₂Si single phase was formed, and no obvious Mg, Si, MgO and SiO₂ peaks are detected from XRD, as is shown in Figure.3. Phases of microwave samples at 903K (microwave power=3.5kW) show that some MgO and SiO₂ peak appear, as is shown in Figure.4. It can be attributed to the easier oxidation of Mg at higher temperature. So, the optimum temperature of solid-state synthesis by microwave is about 853K, which Mg and Si react completely and nearly no obvious oxidation is detected.

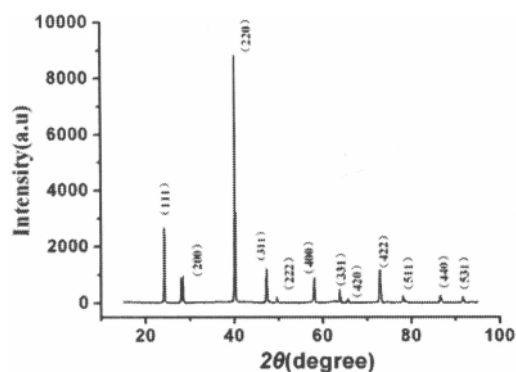


Figure 3. XRD patterns of Mg₂Si samples (power=2.5kw)

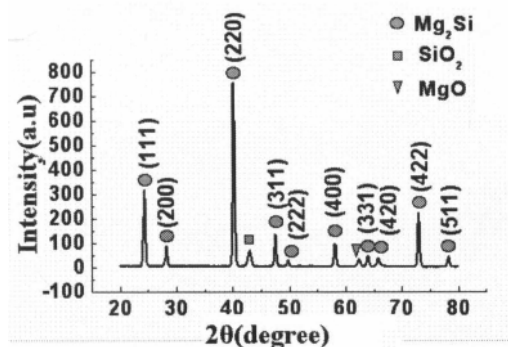


Figure 4. XRD patterns of Mg₂Si samples (power=3.5kw)

3.3 Effect of isothermal holding time on Mg₂Si compounds

Figure.5 shows XRD analysis of various holding-times of Mg, Si powder of stoichiometric proportion at 853K in microwave oven. The phase analysis of the XRD patterns reveals that Mg₂Si is the major phase in the sample. It shows that complete reaction has been carried out

when the holding-time is only 30 minutes. The peaks are very sharp at this situation and no obvious MgO peak appears. However, MgO and SiO₂ impurity peaks appears when the holding-time is 40 minutes as is shown in Figure.5 (b). When the holding-time is only 20 minutes, there are a small amount of Mg peaks of raw powder, as is shown in Figure.5(a). So, the optimum holding-time is 30 min and the excessive content of Mg is essential to compensate the volatilization of Mg during the processing.

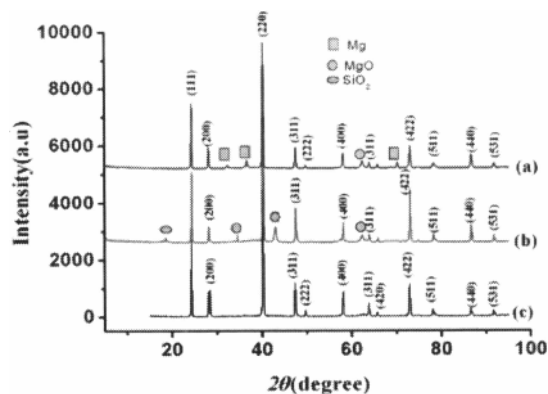


Figure 5. XRD patterns of Mg₂Si samples of different holding-times during synthesis processing (a)—20min; (b)—40min; (c)—30min

4 Conclusions

a) The temperature-rising rate is also dependent on the initial green density. Higher green density provides lower heating rate while power setting are fixed. Irrespective of the green density, all the compacts attain the same steady-state temperature.

b) The optimum parameters by microwave heating to synthesize Mg₂Si from Mg and Si raw powders are 853 K and the holding-time of 30 minutes with the excessive content of 8at% Mg from the stoichiometric ratio.

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