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ScienceDirect
Trans. Nonferrous Met. Soc. China 21(2011) 1785−1789
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Microwave direct synthesis and thermoelectric properties of Mg_2Si by solid-state reaction

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Received 20 August 2010; accepted 14 February 2011

Abstract: In order to reduce the oxidation and volatilization caused by Mg element in the traditional methods for synthesizing Mg_2Si compounds, Mg_2Si thermoelectric materials were prepared by solid state reaction and microwave radiation techniques. Structure and phase composition of the materials were investigated by X-ray diffraction. The electrical conductivity, Seebeck coefficient and thermal conductivity were measured as a function of temperature from 300 to 700 K. It is found that high purity Mg_2Si powders can be obtained with excessive content of 8% Mg from the stoichiometric Mg_2Si at 853 K and 2.5 kW for 30 min. A maximum dimensionless figure of merit, *ZT*, of about 0.13 was obtained for Mg_2Si at 600 K.
Key words: Mg_2Si; thermoelectric materials; solid state reaction; microwave synthesis

1 Introduction

Magnesium silicide (Mg_2Si) with a face-centered-cubic type structure has been identified as a promising thermoelectric material for power generation in a temperature range from 500 to 800 K [1−4]. Because of the environmental-friendly advantages, such as the abundance of its constituent elements in the earth crust and the non-toxicity of processing by-products, more and more researchers have paid much attention to those compounds [5−6].

However, the phase purity and microstructure of the product Mg_2Si are difficult to control by conventional techniques because of the easy volatilization and oxidation of Mg and the great discrepancy of melting point between Mg and Si. Many synthesis methods have also been applied to Mg_2Si-based compounds to improve their thermoelectric properties, such as vacuum melting [4], solid state reaction [7], mechanical alloying [8−10] and spark plasma sintering (SPS) [3, 11]. Mechanical alloying (MA) or ball milling usually takes a long time and the samples may be contaminated and oxidized even in a protective atmosphere during the milling process. Vacuum melting is difficult to control the synthesis and constituents, the adjustment of structure and performance of the materials because of some problems such as the evaporation and oxidation of Mg, the unevenness or segregation caused by different melting points and different density of Mg from Si. However, the issues above have not been solved radically yet.

These problems mentioned above motivate 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 radiation method at a considerably lower temperature and in a shorter time than the conventional methods [12−14]. The rapid synthesis may lead to smaller grain size and consequently better mechanical properties to improve the product uniformity. Until recently, microwave processing has been mostly restricted to ceramics, cemented carbides and ferrites [13]. Applicability of microwave sintering to 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.

Foundation item: Project (2009BB4228) supported by the Natural Science Foundation Project of Chongqing Science and Technology Commission, China; Project (CK2010Z09) supported by the Research Foundation of Chongqing University of Science and Technology, China
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DOI: 10.1016/S1003-6326(11)60931-X

This led to the use of microwaves to consolidate a range of particulate metals and alloys [15]. This is very interesting from the applicative point of view.

In this work, Mg_2Si thermoelectric materials were prepared by microwave-assisted activation synthesis. It is a rapid process and results in a pure phase material. The results obtained seem to be very interesting and stimulate further research in this direction.

2 Experimental

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

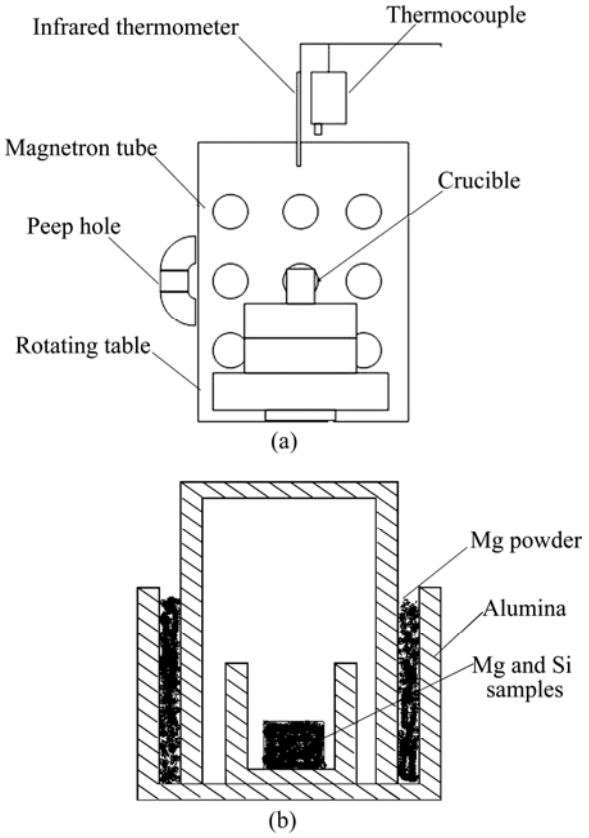

Fig. 1 Schematic diagrams of microwave system setup (a) and crucible (b)

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. According to the stoichiometric proportion of Mg_2Si, Mg (>99.5% purity, 74 μm) and Si (>99.5% purity, 44 μm) with molar ratio of 2.08:1 were used as raw materials. The required amount of these materials was well mixed by an ultrasonic homogenizer in ethanol for 45 min. After being completely dried in the cabinet, they were compressed to form pellets with dimensions of d20 mm×10 mm under appropriate pressure. The samples were then placed in an 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 2.45 GHz microwave generator with continuous adjustable power output of 0−15 kW. An infrared pyrometer was used (Raytek, Marathon series) for temperature measurement. Microwave heating used in the present work was carried out at power level of 2.0−3.5 kW and heated to a designed temperature (580−600 °C), then kept at this temperature (with power level of 1.0−1.5 kW) for 20−40 min. The samples were cooled to room temperature for further control experiment.

Phases of the fabricated materials were detected by X-ray diffraction (D/Max-IIIA) with Cu K_α radiation (λ =0.154 06 nm). The electrical conductivity (σ) and Seebeck coefficient (α) were simultaneously measured by the four-probe dc method in helium atmosphere from room temperature to 800 K using a computer-assisted device. The errors of the Seebeck coefficient and the electrical resistivity measurements were estimated to be less than ±5%. The thermal diffusivity (D) and the specific heat capacity (c_p) of the samples were measured by a laser flash apparatus (Netzsch LFA 457) and a thermal analyzer (Netzsch DSC 404), respectively. The thermal conductivity k was calculated from the relationship $k=\rho Dc_p$, where ρ is the density of the material, measured using Archimedes method at room temperature. Relative density of the compacts measured by Archimedes method was about 96% of the theoretical value.

3 Results and discussion

3.1 Effect of microwave power on Mg_2Si compounds

In order to find out the complete reaction temperature of Mg and Si to form Mg_2Si in microwave chamber, the raw mixed powders are sintered by microwave at temperature from 573 to 903 K. When the input power is kept constant at 2.5 kW and 853 K, Mg_2Si single phase is formed, and no obvious Mg, Si, MgO and SiO_2 peaks are detected from the XRD patterns, as shown in Fig. 2. Phases of microwave sintered samples at 3.5 kW and 903 K show that some MgO and SiO_2 peaks appear, as shown in Fig. 3. It can be attributed to the easier oxidation of Mg at higher temperature. Thus, the optimum temperature of solid-state synthesis by

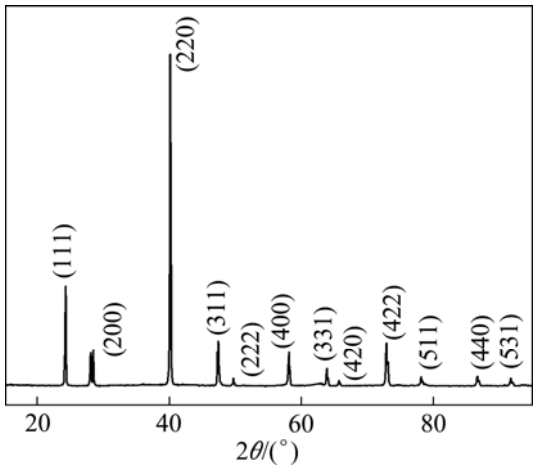

Fig. 2 XRD pattern of Mg_2Si sample sintered at microwave power of 2.5 kW

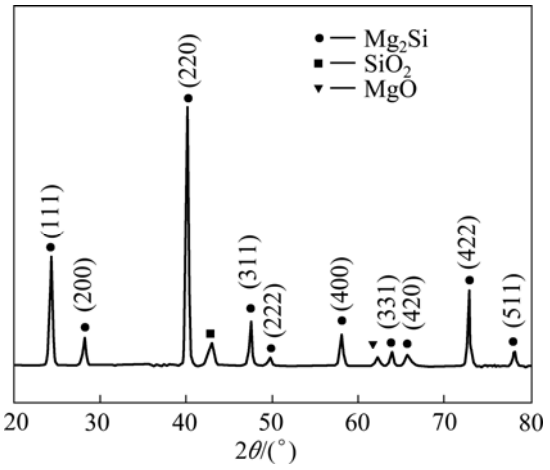

Fig. 3 XRD pattern of Mg_2Si sample sintered at microwave power of 3.5 kW

microwave is about 853 K, at which Mg and Si react completely and nearly no obvious oxidation is detected.

3.2 Effect of isothermal holding time on Mg_2Si compounds

Figure 4 shows the XRD patterns of Mg and Si powders on stoichiometric proportion at 853 K in microwave oven for various holding time. The phase analysis of the XRD patterns reveals that Mg_2Si is the major phase in the sample, and complete reaction takes place when the holding time is only 30 min. The peaks are very sharp at this situation and no obvious MgO peak appears. However, MgO and SiO_2 impurity peaks appear when the holding time is 40 min. When the holding time is only 20 min, there are a small amount of Mg peaks of raw powder. Thus, the optimum holding time is 30 min and the excessive content of Mg is essential to compensate the volatilization of Mg during processing.

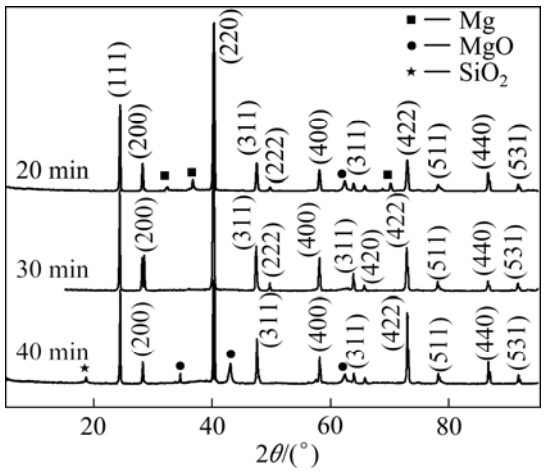

Fig. 4 XRD patterns of Mg_2Si samples with different holding time during synthesis processing

3.3 Thermoelectric properties of Mg_2Si compound

The temperature dependence of electrical conductivity of the samples are shown in Fig. 5. In all the samples, the electrical conductivity increases monotonically with temperature in a range of 300−700 K, indicating semiconduction behavior [16].

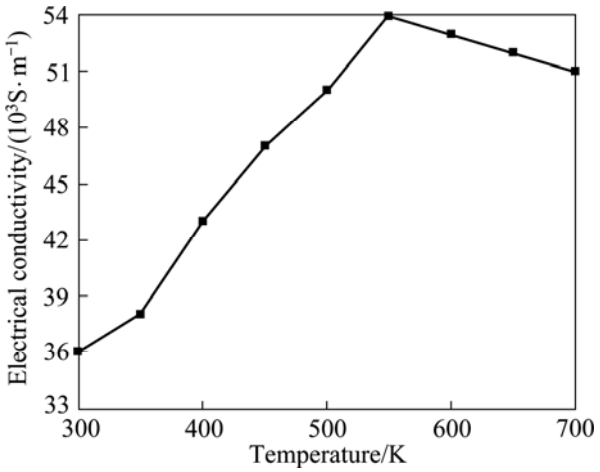

Fig. 5 Variation of electrical conductivity with holding temperature for Mg_2Si compounds

Figure 6 shows the variation of Seebeck coefficient with holding temperature of Mg_2Si. The Seebeck coefficient for Mg_2Si compound increases with temperature, and reaches the lowest value of −440 μV/K at about 550 K, and then decreases at higher temperature mainly due to the occurrence of an increasing number of thermally excited minority carriers. A negative Seebeck coefficient suggests that the obtained materials exhibit n-type conductivity.

The variation of thermal conductivity for Mg_2Si compound k with the holding temperature is also

depicted in Fig. 7. The overall thermal conductivity k is given by $k=k_e+k_{ph}$, where k_e is the electronic thermal conductivity and k_{ph} is the lattice thermal conductivity. k_e is related to electrical conductivity by Wiedemann-Franz law as:

$$k_e=L_0\sigma T$$

where L_0 is Lorenz number. For the degenerate conduction, $L_0 = 2.45\times10^{-8}$ V^2/K^2 is used. k_{ph} can be obtained by subtracting k_e from the total thermal conductivity. For Mg_2Si compounds, k_{ph} is 75%−96% of k. k_{ph} gives essential contribution, indicating phonon-phonon interactions are the primary sources of thermal resistance [17].

The temperature dependence of the dimensionless figure of merit $ZT=(\alpha^2\sigma/k)T$ of Mg_2Si compound is presented in Fig. 8. With the increase of temperature, the ZT value of Mg_2Si compounds increases. A maximum figure of merit ZT = 0.13 is obtained for Mg_2Si at about 600 K.

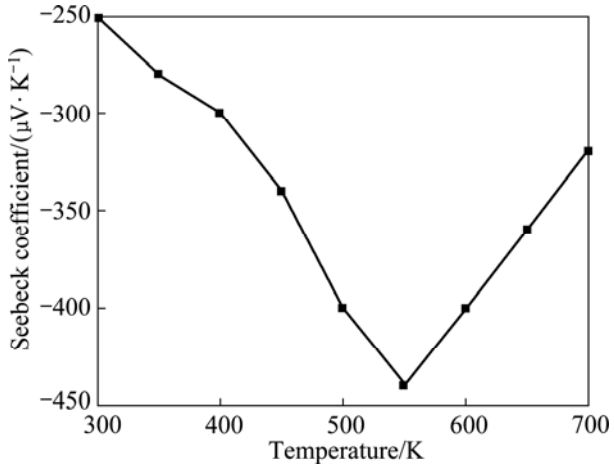

Fig. 6 Variation of Seebeck coefficient with holding temperature for Mg_2Si compounds

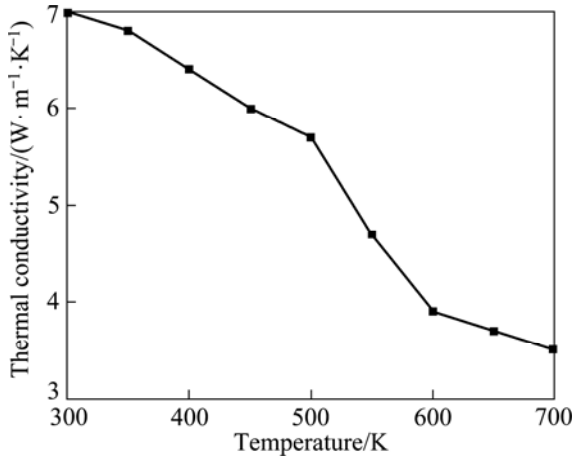

Fig. 7 Variation of thermal conductivity with holding temperature for Mg_2Si compound

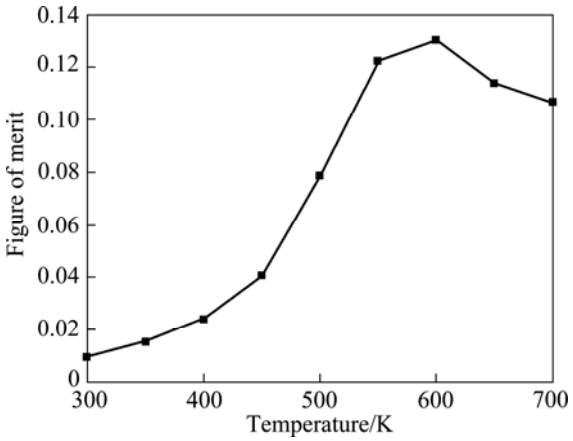

Fig. 8 Temperature dependency of figure of merit, ZT, for Mg_2Si compound

4 Conclusions

1) The optimum parameters of microwave heating from Mg and Si raw powders to synthesize Mg_2Si are heating temperature of 853 K, holding time of 30 min with an excessive content of 8% Mg from the stoichiometric ratio.

2) With the electrical conductivity, Seebeck coefficient and thermal conductivity are measured from room temperature to 700 K, the dimensionless figure of merit is calculated and discussed. The highest ZT value is 0.13 at 600 K for Mg_2Si compound. It is also demonstrated that microwave-assisted synthesis technique is a suitable method for preparing Mg_2Si thermoelectric materials.

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Mg_2Si 的微波固相合成及其热电性能

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摘 要：为了解决 Mg_2Si 传统制备方法中 Mg 的氧化、挥发等问题，采用微波低温固相反应法合成 Mg_2Si 热电材料。用 XRD 分析手段研究合成产物的结构及相组成。在 300 到 700 K 的温度范围内，对材料的电导率、Seebeck 系数和热导率随温度的变化进行测量。 结果表明，当 Mg 过量 8%、加热功率为 2.5 kW 时，于 853 K 保温 30 min，可以得到单相 Mg_2Si 热电化合物。在测试温度范围内，Mg_2Si 具有较高的品质因数 *ZT* 值，在 600 K 温度下达到 0.13。

关键词: Mg_2Si；热电材料；固相反应；微波合成

(Edited by FANG Jing-hua)