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Low temperature synthesis of forsterite from hydromagnesite and fumed silica mixture

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Abstract

Forsterite was prepared via solid-state reaction by using hydromagnesite (basic magnesia carbonate) and fumed silica, aiming at completing the reaction $2MgO+SiO_2 \rightarrow Mg_2SiO_4$ at low calcination temperature. The phase development and morphology evolution of the hydromagnesite and hydromagnesite–fumed silica mixture during heat treatment were characterized by means of scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) nitrogen-gas adsorption method, and X-ray powder diffraction (XRD). A diffusion distance of less than 300 nm for Mg^{2+} and Si^{4+} for forsterite formation was obtained because the formed high reactivity MgO with the nanosheet structure of its parental hydromagnesite and the fumed silica with particle size of less than 100 nm were homogeneously mixed. Monolithic forsterite was synthesized after calcination of the hydromagnesite–fumed silica mixture at 1100 °C.

Keywords: A. Calcination; A. Powders: solid state reaction; B. Electron microscopy; D. Silicate

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1. Introduction

Forsterite ($2MgO \cdot SiO_2$) has a high melting point (1890 °C), high temperature creep resistance, low thermal conductivity, and thus excellent insulation properties [1,2]. Therefore, forsterite is of interest to the high temperature ceramic industry [2,3]. Besides, forsterite-based ceramics can also be used as a medium for tunable lasers [1,4] due to its good refractoriness, chemical stability, and excellent insulation properties even at high temperatures [1]. Various approaches, such as co-precipitation [5], polymer precursor [6], sol–gel [7,8] and mechanical activation [9–11], have been employed in order to produce high purity and high reactivity forsterite powders at low calcination temperature because the reactivity of the prepared powder strongly depends on the firing temperature [12,13]. The calcination temperatures for forming phase-pure forsterite have been reported to be around 800 °C by co-precipitation [5], polymer precursor [6] and citrate–nitrate routes (sol–gel method) [7], above 1000 °C by heterogeneous sol–gel [8] and 1000–1200 °C using mechanochemical activation [9–11]. However, these methods cannot be used to produce forsterite for large-scale industrial applications due to their high cost.

Forsterite can be industrially prepared with a large quantity using simple and cheap heat treatment methods based on the solid-state reaction synthesis (mixed oxide synthesis method [14]), using MgO- and SiO_2-bearing compounds as precursors [12,13,15]. However, in such a process, a $Mg_2SiO_4/MgSiO_3$ layer would be initially formed between the magnesia and silica particles [15] and Mg^{2+} and Si^{4+} need to diffuse through this intervening $Mg_2SiO_4/MgSiO_3$ layer during heat treatment [15]. To overcome the kinetic constraints, high calcination temperatures (up to 1400 °C) and/or long soaking times (up to 24 h) are needed [12]. Therefore preparation of forsterite via solid state reaction usually increases grain growth and aggravates particle agglomeration, and consequently leads to a poor sinterability of the forsterite powder [12,13].

Hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) has been widely used for the synthesis of high reactivity MgO powders [16–18]

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because hydromagnesite has a sheetlike structure with a sheet thickness of less than 50 nm [16,17]. Calcination of the compound at appropriate low temperatures (500–700 °C) produces MgO with almost the identical morphologies of the hydromagnesite precursor, with lots of edges, corners, step edges, step corners and, in particular, vacancies [19]. When fumed silica with particle size of less than 200 nm is homogeneously mixed with the hydromagnesite the diffusion distance for forming forsterite would be less than 300 nm between the SiO_2 and the formed high reactivity MgO particles [16–18], and consequently the complete forsterite formation could be accomplished at lowered temperatures. Therefore, the objective of this work is to synthesize forsterite at a low firing temperature through conventional solid-state reaction with hydromagnesite and fumed silica as starting materials and thus making the resulting forsterite powder with high reactivity more affordable to the industrial application.

2. Experimental

Powders of hydromagnesite (basic magnesium carbonate, MgO: 44.9 wt%, d_{50}=7.1 μm, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and fumed silica (SiO_2, ≥99.8 wt% purity, specific area=380 $m^2\ g^{-1}$, Guangzhou GBS Science and Technology Industrial Co. Ltd., Guangzhou, China) were mixed with a molar proportion corresponding to forsterite ($2MgO \cdot SiO_2$) for 12 h in ethanol in a rotary mill, using zirconia balls of 5 mm diameter with a balls/powder weight ratio of 3/1. The obtained hydromagnesite–fumed mixture and hydromagnesite powders were calcined in a temperature range from 700 to 1100 °C for 3 h.

Phases and extents of reactions of the hydromagnesite powders and hydromagnesite–fumed silica mixture were examined with X-ray powder diffraction (XRD; 3003-TT, Seifert, Ahrensburg, Germany) using Cu Kα (40 kV, 40 mA) radiation. Microstructural analysis was carried out by scanning electron microscopy (SEM; XL 30 FEG, Philips, the Netherlands) at 10 kV. High-resolution SEM observation of the hydromagnesite powder after calcining at 1100 °C was performed using a Nova Nano SEM 450 (Philips, the Netherlands) operating at 5 kV. The specific surface area of the hydromagnesite powders before and after heat treatment and the calcined hydromagnesite–fumed silica mixture was determined by the Brunauer–Emmett–Teller nitrogen-gas adsorption method (BET, TriStar 3000 V, Micromeritics Instrument Corp., USA) after drying at 150 °C for 12 h.

3. Results and discussion

Fig. 1 shows the crystallinity and phase development of the hydromagnesite powders during heat treatment. All the diffraction peaks were indexed to the monolithic hydromagnesite phase ($4Mg(CO)_3 \cdot Mg(OH)_2 \cdot 4H_2O$) of the starting hydromagnesite powders before heat treatment. Broadened and low intensity MgO (periclase) peaks were observed after the hydromagnesite was fired at 700 °C and 800 °C. During hydromagnesite decomposition the oxygen and magnesium ions in the formed MgO occupy the same sites in the crystal lattice of hydromagnesite, generating a pseudomorphous phase of hydromagnesite [18]. Consequently, the formed MgO from hydromagnesite decomposition exhibited small crystal size and severely distorted intrinsic structure at 700 °C and 800 °C. With the calcination temperature increase from 800 °C to 1100 °C the peaks corresponding to MgO were gradually increased and narrowed, due to the crystal structure perfection and crystal growth of the formed MgO during heat treating.

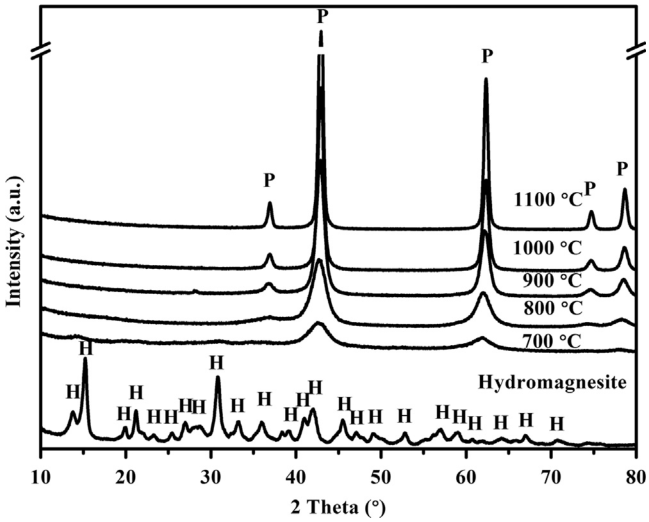

Fig. 1. X-ray diffraction patterns of the hydromagnesite powder after heat treatment at different temperatures (H, hydromagnesite ($4Mg(CO)_3 \cdot Mg(OH)_2 \cdot 4H_2O$), powder diffraction file No. 01-070-0361; P, periclase (MgO), powder diffraction file No. 01-077-2364).

Fig. 2 illustrates the BET specific surface area change of the hydromagnesite powders during heat treatment. It can be seen from Fig. 2 that the specific surface area increases from 22.4 $m^2\ g^{-1}$ of the initial hydromagnesite to 51.1 $m^2\ g^{-1}$ after firing at 700 °C and maximizes to 144.4 $m^2\ g^{-1}$ at 800 °C. As indicated in Fig. 1, the formed MgO has highly distorted crystal structure after firing at 700 °C and 800 °C. The high specific surface area and distorted crystalline structure of the calcined hydromagnesite powders imply that the formed MgO has a high reactivity at 700 °C and 800 °C. With further increase of the firing temperature, the specific surface areas decreased to 100.1 $m^2\ g^{-1}$ at 900 °C, 64.2 $m^2\ g^{-1}$ at 1000 °C and 37.0 $m^2\ g^{-1}$ at 1100 °C. This is believed to be caused by the grain/crystal growth of MgO (Fig. 1).

Phase development of the mixture during calcination is shown in Fig. 3. For heat treating of the sample at 700 °C only low and broadened periclase intensities were observed in the mixture. Forsterite peaks begin to appear at 800 °C, which is in line with the DTA results (not shown here) where the exothermic peak at 858 °C is assigned to the massive forsterite formation. With increasing calcination temperature from 800 °C to 1000 °C the forsterite peaks increase in height at the expense of the MgO (periclase) (Fig. 3), as the result of the solid-state reaction between the formed reactivity MgO and SiO_2. On further increasing temperature to 1100 °C, MgO totally disappeared and single crystalline forsterite was obtained.