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Microwave-assisted synthesis and characterization of $Nd_{1.5}Mg_{17}Ni_{0.5}$–Fe_3O_4 hydrogen storage composite

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ABSTRACT

This work reports the preparation of $Nd_{1.5}Mg_{17}Ni_{0.5}$–Fe_3O_4 hydrogen storage composite in a single mode 2.45 GHz microwave cavity. The physicochemical properties (thermodynamic and kinetic characteristics, hydrogen absorption/desorption properties, thermal behavior, phase composition and morphology) were characterized by pressure-composition isotherms, differential scanning calorimetry, X-ray diffraction, scanning electron microscope with an energy dispersive X-ray spectrometer, transmission electron microscopy, and laser granulometry. The proposed microwave synthesis, in contrast with conventional sintering method, offers rapid heating, makes homogenous composition and hence improves the hydrogen storage properties of the composite.

1. Introduction

The storage of large quantities of hydrogen under safe pressure is a key factor in establishing a hydrogen-based economy [1]. So a broad variety of materials are considered as potential hydrogen-storage materials [2] such as nanostructural carbon [3], tuning clathrate hydrates [4], metal organic frameworks [5], metal hydrides [6], lithium and sodium amidoboranes [7]. According to the International Energy Association's (IEA) feasibility study, the mobile hydrogen storage system can provide a gravimetric storage capacity larger than 5 wt.% of H_2, desorption temperature lower than 423 K and at least 1000 hydriding/dehydriding cycles life [8]. Magnesium is the only pure metallic element that can reversibly store more than 5 wt.% H in the form of metal hydride. It is the lightest of all engineering metals with a density of 1.74 g/cm^3 and the sixth most abundant element in the earth crust. However, its disadvantages are poor hydrogen sorption kinetic properties, high sorption temperature and high reactivity to oxidation. Many efforts have been made to improve its hydriding/dehydriding performance. For example, many elements such as V, Ti, Ni, Fe, Mn, Cu and Ag [9–11] have been selected as additives to magnesium. Among the addition of catalysts [6], pure transition metals [9] and oxides [12] are often reported. Re–Mg–Ni alloys always showed excellent hydrogen storage property. Xie et al. [13] prepared hydrogen storage alloys $Mg_{2-x}Nd_xNi$ ($x = 0$, 0.1, 0.2, 0.3) by vacuum induction melting under the high purity helium atmosphere and found that the substitution of Nd for Mg had obviously improved the hydrogen storage properties of Mg_2Ni. According to the results in literatures, transition metal oxides show higher potential. Oxides are cheap, and low amounts already have a substantial effect. Huang et al. [14] investigated iron oxides (Fe_2O_3, Fe_3O_4) as catalysts for improving hydrogen sorption in Mg-based materials and reported that the composite material containing Fe_3O_4 showed the higher hydrogen storage capacity than the material with Fe_2O_3 because of the reduction reaction between magnesium and iron oxides.

Additionally, the preparation of Mg-based composite is one of the key issues since it has strong influence on the microstructure, morphology and macro-properties of the material. The conventional heating method of thermal conduction from the outside to the inside of the sample need more time to heat specimens completely, cannot heat samples uniformly because of the thermal gradient and may lose much thermal energy during thermal conducting. A synthesis route encompassing encapsulation of subliming Mg by La from all sides has been adopted by Dutta and Srivastava [15], who melted La_2Mg_{17} intermetallic in a pre-baked quartz tube under an argon atmosphere with the help of a radio-frequency induction furnace. It is a pity that a special precaution coming from the very high Mg vapor pressure at the temperature of the melting point of La element was unreachable. It is well known that some external fields usually have significant effect on the properties of materials, especially for metal materials [16]. We recently carried out a feasibility study on synthesis of Mg–3 mol%$LaNi_3$ composite prepared under an external magnetic field and preparation of Mg_2NiH_4 made by microwave-assisted activation synthesis from

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micro-particles [17,18]. Compared with conventional processes, sintering under an external magnetic field and microwave field has attracted increasing attention due to their significant advantages in material processing. Microwaves allow volumetric heating of materials. Microwave energy transforms into heat inside the material, which results in significant reduction of energy and processing time. Investigations on microwave sintering of metallic materials primarily focused on ferrous [19], copper-based alloys [20], aluminum and its composites [21] have been reported and the results indicated that microwave sintering was superior to the conventional sintering in elevating sintered density and improving microstructural uniformity.

The aim of the present study has two aspects (i) to evaluate the feasibility of microwave sintering approach for synthesizing $Nd_{1.5}Mg_{17}Ni_{0.5}$–Fe_3O_4 composite and (ii) to investigate the effects of microwave sintering on the microstructure, hydriding/dehydriding thermodynamic and kinetic properties of this composite.

2. Experimental details

2.1. Preparation

The initial materials used in the experiments were Nd (>99.5% pure, ~200 mesh), Mg (>99.5% pure, ~400 mesh), Ni (>99.5% pure, <400 mesh) and Fe_3O_4 (>99.5% pure, ~200 mesh) powders. The as-received elemental powders of Nd, Mg and Ni with the atom ratio as 1.5:17:0.5 were mixed with 5 wt.% Fe_3O_4 powder. All the powders were milled in planetary ball milling with 60 rpm before sintering. To prevent oxidation during ball milling process, the samples contained in ball milling tanks were put in the glove box in a gas mixture of 95%Ar + 5%H_2. The tankage in this experiment is 80 cm^3 and the weight ratio of grinding media to material is 8:1. They were pressed under 300 MPa for 5 min into compact with dimension of 15 mm diameter and 5 mm thickness by a uniaxial single-acting press.

To verify that microwaves contribute effectively to the heating of the samples, the tests of sintering with and without microwave furnace were performed. The composite synthesized without microwave field is labeled as specimen 1 (S1) while the other with external microwave field is specimen 2 (S2). Microwave sintering was carried out in a microwave furnace with a frequency of 2.45 GHz microwave generator, a power output continuously adjustable from 0 to 3 kW, a cylindrical single-mode tuneable applicator, and a computer control system. Temperature was measured by an infrared pyrometer with an emissivity of 0.75. The compact was placed in the center of alumina fiber insulations with supplementary SiC heater. The alumina fiber insulations were used and mounted encircling the compact to inhibit the heat loss. The heating rate was adjusted by changing the output power. The whole sintering process was in high purity argon under an ambient pressure. Specimen 2 was sintered under the external microwave field with the heating rate of 40 K/min and was kept at 943 K for 15 min with flowing 0.1 MPa Ar. Similarly, sintering was conducted in a tubular resistance furnace without microwave field for specimen 1. The products were cooled to room temperature and crushed into micro-particles for the characterization. Fig. 1 shows a schematic illustration of the experimental equipment. It mainly consists of a microwave oven and a heat preservation system.

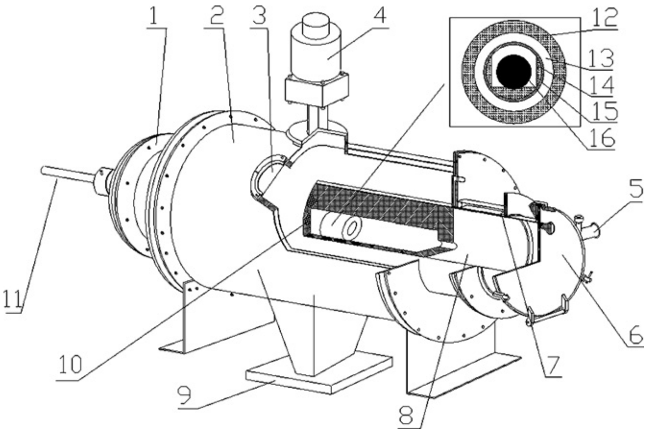

Fig. 1. Schematic illustration of apparatus for the microwave furnace: (1) venthole, (2) furnace body, (3) peephole, (4) agitator, (5) vacuum system, (6) furnace door, (7) O-ring seal, (8) furnace tube, (9) microwave feed-in, (10) insulating course, (11) infrared pyrometer, (12) insulation fiber, (13) alumina insulation, (14) corundum crucible, (15) supplementary SiC heater, and (16) sample.

2.2. Characterization

The samples were activated for 3 times (under 4.0 MPa H_2, absorption for 60 min, and desorption in vacuum for 60 min at 573 K). The pressure-composition isotherm (PCT) and kinetic properties were measured by a volumetric method according to Sievert's law using automatic apparatus from SUZUKI HOKAN Co., Ltd. in Japan. The structures of the samples were analyzed by X-ray diffraction (XRD) and their morphologies were studied by scanning electronic microscopy (SEM) with an energy dispersive X-ray analysis system (EDS). The TEM image of product was obtained at the accelerating voltage of 200 kV. TEM samples were prepared by the room temperature organic (RTO) method [22]. Size measurements were performed using a Malvern Mastersizer hydro 2000S in liquid ethanol media. The sample (20 mg) was dispersed in ethanol using an ultrasonic device (80 kHz, 150 W, 20 min). Differential scanning calorimeter (DSC) measurements were carried out on approximately 30 mg of as-prepared sample at a heating rate of 6 K/min from 298 to 773 K and the maximum temperature was kept for 120 min with flowing 0.1 MPa Ar at a rate of 100 ml/min.

3. Results and discussion

3.1. The structural characteristics

The XRD patterns of specimens 1 and 2 before and after hydriding reaction are shown in Fig. 2. Apart from the starting iron oxides (Fe_3O_4, JCPDS 19-0629, 28-0491) in the composites, peaks of the

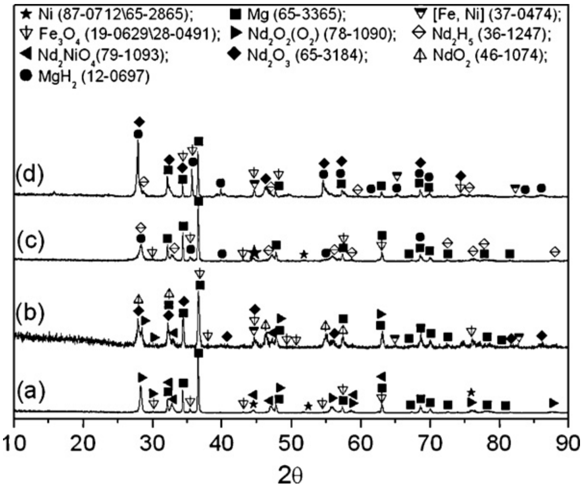

Fig. 2. X-ray diffraction patterns of $Nd_{1.5}Mg_{17}Ni_{0.5}$–Fe_3O_4 prepared with and without external microwave field before (a for S1, b for S2) and after (c for S1, d for S2) hydride activation.