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Combustion synthesis of TiFe by utilizing magnesiothermic reduction

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ABSTRACT

This paper describes a new method for producing TiFe hydrogen storage alloy through combustion synthesis by utilizing the magnesiothermic reduction reaction. The reaction mechanism and the effects of a gaseous atmosphere and pressure on the purity of TiFe products and their hydrogen storage properties were examined in this study. In the experiments, Fe, TiO_2, and Mg were used as raw materials and were mixed in a molar ratio of 1:1:4. The mixture was compacted and then heated in a normal or pressurized atmosphere of hydrogen and argon. Temperature changes with time were measured, and the obtained results indicated that the melting of magnesium triggered the reaction. X-ray diffraction analysis revealed that highly pure TiFe could be synthesized in a pressurized atmosphere, containing both hydrogen and argon. The products synthesized in such a pressurized atmosphere stored approximately 1.0 mass% hydrogen and indicated flat plateaus. The process proposed in this study showed the possibility of being a new attractive production method for TiFe hydrogen storage alloy.

1. Introduction

The titanium iron (TiFe) alloy is well known as one of the most attractive hydrogen storage alloys because of its good cycling property, reversibility of absorption/desorption under normal conditions and the abundance of raw materials [1]. However, for practical use, TiFe requires a severe activation treatment because an oxidation film is always generated on its surface and prevents TiFe from storing hydrogen. Many researches on such activation treatments have been reported [2–7]. In a typical activation treatment, the pulverized alloy is heated to a high temperature (over 623 K) in vacuum, and is then pressurized with hydrogen at 4.0 MPa in order to allow hydrogenation. Generally, TiFe acquires sufficient ability to store hydrogen at ordinary temperatures after the repeating procedures of hydrogenation and dehydrogenation more than 10 times. Many researches concerned with improving the initial activation of TiFe have been reported, among which doping TiFe with a third element such as Mn, V, O, or Ti is a considerably popular method [8–12]. However, there have been few researches focusing on finding new production methods for TiFe. In general, TiFe is produced using metallic titanium and iron by means of arc or induction melting. It is difficult for the wide application of TiFe since metallic titanium is expensive and the conventional production processes consume a significant amount of time and energy. It is well known that the melting point of titanium is as high as 1943 K and the subsequent homogenization requires high temperature and a long time as well. Saito et al. reported the production of TiFe alloy by carrying out homogenization at a temperature of 1273 K for 24 h [13]. Mechanical alloying (MA) is an attractive method for synthesizing some intermetallic compounds without any melting process. Zadorozhnyy et al. successfully synthesized TiFe alloy by ball milling [14], which used highly pure and expensive metallic titanium powder as raw material. Molten salt electrolysis is another method for synthesizing TiFe intermetallic compound. Panigrahi et al. synthesized TiFe intermetallic compound using mixed ilmenite and titanium dioxide by electrochemical reduction in molten calcium chloride. [15] They found that highly pure TiFe could be produced using only ilmenite by direct electrochemical reduction at a constant voltage of 3.0 V. However, this process required a long time of 25 h to synthesize TiFe and the current efficiency was as low as 8%.

Hydriding combustion synthesis (HCS) and self-ignition combustion synthesis (SICS) techniques have been employed to synthesize some TiFe-based hydrogen storage alloys. Saita et al. synthesized TiFe from well-mixed fine powders of metallic titanium and iron in a pressurized hydrogen atmosphere using the HCS method [16]. TiFe synthesized by this method stored hydrogen as much as 1.7 mass%, which is about 95% of the theoretical capacity. Wakabayashi and Yasuda et al. reported the production of TiFe, $TiFe_{1-x}Mn_x$, and oxygen-doped TiFe by using the SICS method [9,10,17]. In their methods, mixed powders with desired compositions were uniformly heated up in a pressurized hydrogen atmosphere to directly synthesize TiFe alloys. In these processes,

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expensive metallic titanium powders were used raw material. Recently, Tsuchiya et al. reported combustion synthesis of TiFe from iron and titanium dioxide powders by utilizing the calciothermic reduction [18]. The raw materials used in this method were cheaper than those in MA, HCS, and SICS processes, and titanium oxide was used directly to replace metallic titanium. Furthermore, this method is quite time-saving as the combustion synthesis finished in several minutes. However, the as-used reducing agent of calcium powder is expensive. In this study, as an alternative reducing agent to substitute metallic calcium, metallic magnesium powder is used. Nersisyan et al. have synthesized Ti powders containing a small amount of oxygen from titanium dioxide through combustion synthesis directly utilizing magnesiothermic reduction [19,20].

Eqs. (1) and (2) represent the reduction reactions by using calcium and magnesium, respectively. The released heat is higher for the calcium-based reaction than that using magnesium. This study focuses on the possibility of producing TiFe alloys using magnesium as reducing agent and characterizing their hydrogen storage properties.

$$TiO_2 + Fe + 2Ca = TiFe + 2CaO + 366\ kJ \tag{1}$$

$$TiO_2 + Fe + 2Mg = TiFe + 2MgO + 299\ kJ \tag{2}$$

2. Experimental

Fig. 1 shows a schematic diagram of the experimental apparatus from the side and top views. The reactor contained a water-cooled stainless steel chamber with a reactor and a graphite heater inside the chamber. Two R-type thermocouples were used for controlling the heater temperature and for measuring the sample temperature. The heater could uniformly heat a sample up to 1773 K in a high-pressure (up to 1.0 MPa) hydrogen or argon atmosphere. The pressure inside the reactor was maintained constant by using an automatic on/off controller.

Commercially available reagents of TiO_2 (99.9%, 2 μm pass), Fe (99.9%, 3–5 μm), and Mg (99.9%, 180 μm) powders, from Kojundo Chemical Laboratory Co., Ltd, were used in our experiment. A total mass of 40 g of these reagents was mixed in a molar ratio of TiO_2:Fe:Mg = 1:1:4. In order to accelerate the reduction of TiO_2, the amount of Mg used was twice of the theoretical value calculated from Eq. (2).

At first, TiO_2 and Fe powders were mechanically mixed in acetone by using a homogenizer at room temperature for 20 min. The mixture was then left in a desiccator to dry in air at 383 K for 20 h. Next, Mg was dry-mixed with the TiO_2 and Fe mixture to prevent oxidation or hydroxylation due to the heating in air. Subsequently, 10 g of the mixture including TiO_2, Fe, and Mg was pressed under a pressure of 20 MPa for 5 min to form a cylinder-shaped agglomerate with a diameter of 20 mm. Finally, four pieces of the cylinder were placed in a graphite crucible that was carefully covered by a carbon sheet to prevent the sample from sticking between the crucible and product. Fig. 2 shows the pictures for the four pieces of the cylinders in the graphite crucible before (a) and after (b) combustion. An R-type thermocouple was placed inside a protective magnesia tube which was placed at the center of the sample.

The reactor was evacuated to a pressure below 20 Pa by using a rotary pump, and 99.999% pure argon was then introduced until the pressure increased to 0.1 MPa. After this procedure was repeated three times, hydrogen or argon gas was introduced into the reactor to raise the pressure to 0.1 or 1.0 MPa. Table 1 summarizes the gas atmosphere and pressure conditions for each sample. In our experiment, the samples were uniformly heated using a graphite heater with a temperature ramp of 40 K/min, and the temperature changes in the sample were monitored.

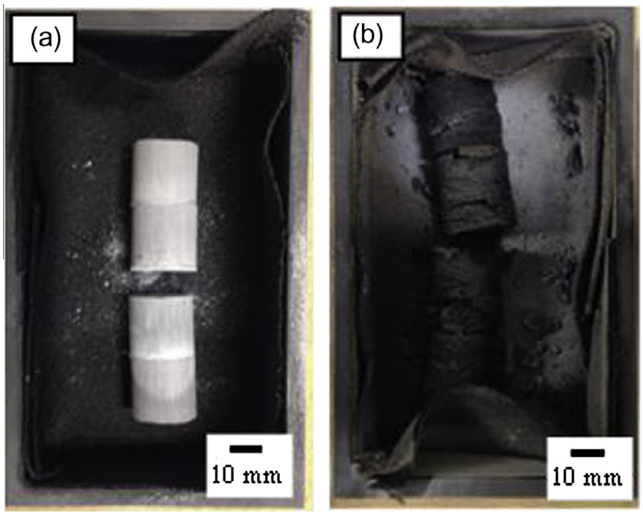

Fig. 2. Photographs of four pieces of cylinder-shaped agglomerates before (a) and after (b) combustion synthesis.

Table 1
Atmosphere and pressure inside the reactor during combustion synthesis for producing four different samples.

Sample name	Atmosphere	Pressure (MPa)
H01	H_2	0.1
H10	H_2	1.0
A01	Ar	0.1
A10	Ar	1.0

As soon as an exothermic reaction was observed, which was detected by a quick temperature jump, the heating of the samples was immediately stopped, and the samples were naturally cooled to room temperature. The products were polished in order to remove the carbon sheet from their surface. After that, the products were purified by magnetic stirring in a 6.3 mass% nitric acid solution for 5 h at a rotation speed of 300 rpm under ambient conditions to remove the magnesium residue and the by-product of magnesium oxide. The products were then left in a desiccator to dry in air at 383 K for 20 h. Finally, the products were treated with 3.6 mass% hydrochloric acid by magnetic stirring for 3 h at a rotation speed of 300 rpm to remove the oxide layer on their surfaces, and then the products were left in a desiccator to dry in air at 383 K for 20 h.

The product phases were identified by X-ray diffraction (XRD) (Miniflex, Rigaku) and the morphology and elemental analysis of the products were observed using a field emission scanning electron microscope (FE-SEM) (JSM-7001FA, JEOL) equipped with an energy dispersive X-ray spectrometer (EDS). The particle size distribution of the products was measured using a laser diffraction scattering apparatus (LA-950, HORIBA). Thermodynamic calculations for the chemical reactions such as that given in Eqs. (1) and (2) were carried out using HSC Chemistry 5.11 software.

Shortly after the washing treatment, the products were placed in a stainless steel reactor to measure their pressure-composition-temperature (PCT) properties calculated by Sievert's method. The PCT properties of the products were evaluated after repetition of the activation treatment for three times. The activation treatment was carried out shortly after the washing treatment, and involved activating and stabilizing the products seven times. In the activation treatment, at first, the

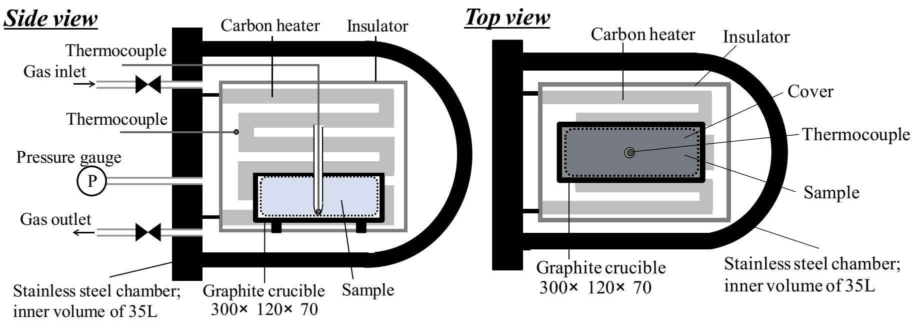

Fig. 1. Schematic diagram of combustion synthesis (CS) reactor [18,21]. Hydrogen (H01 and H10) and argon (A01 and A10) atmospheres were used.