Journal of Alloys and Compounds 480 (2009) 592–595

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Self-ignition combustion synthesis of TiFe in hydrogen atmosphere

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ARTICLE INFO

*Article history:*
Received 15 July 2008
Received in revised form 29 January 2009
Accepted 1 February 2009
Available online 10 February 2009

*Keywords:*
Metal hydrides
Powder metallurgy
Gas–solid reactions

ABSTRACT

This paper describes the *self-ignition combustion synthesis* (SICS) of highly active titanium iron (TiFe) in a high-pressure hydrogen atmosphere without employing an activation process. In the experiments, well-mixed powders of Ti and Fe in the molar ratio of 1:1 were uniformly heated up to 1085 °C, the eutectic temperature of Ti–Fe binary system, in pressurized hydrogen at 0.9 MPa. The electric source was disconnected immediately after the ignition between Ti and Fe, and the mixture was cooled naturally. In this study, the exothermic reaction $Ti + Fe = TiFe + 40\,kJ$ occurred at around 1085 °C after the hydrogenation and decomposition of Ti. X-ray diffraction analysis showed that the final product had only one phase—$TiFeH_{0.06}$—which can store hydrogen of 1.55 mass% under hydrogen pressure of 4 MPa. The product obtained by SICS contained considerably more hydrogen quickly as compared to the commercially available product; this fact can be explained by the porous structure of the obtained product, which was observed using a scanning electron microscope. In conclusion, the SICS of TiFe saved time and energy, yields products with high porosity and small crystals, enabled easy hydrogenation, and did not require activation processes.

## 1. Introduction

The hydrogen storage alloy titanium iron (TiFe) is practically useful since it has good cycling property, low reaction temperature, low plateau pressure, and low production cost [1]. The conventional product, synthesized by arc melting method, needs a time- and energy-consuming activation process. In general activation processes, TiFe is ground to a particle size of 100 mesh or less, which has to be repeated around 10 times, vacuumed at elevated temperatures in the range of 400–500 °C for dehydrogenation, and passed through pressurized hydrogen at 0.7 MPa for hydrogenation [2,3]. However, it is still difficult to charge hydrogen completely because of the contamination of the product surface due to oxidation on exposure to air.

Thus far, several *combustion synthesis* (CS) techniques [4–7] and *hydriding combustion synthesis* (HCS) techniques [8–13] have been reported; in HCS techniques, the well-mixed raw materials are ignited under high-pressure hydrogen to directly produce metal hydrides such as $Mg_2NiH_4$, $Mg_2FeH_6$, and $MgH_2$. These techniques effectively eliminate the need for an activation process in the production of hydrogen storage alloys. In particular, a previous study [14] has revealed that the formation of the liquid phase initiates HCS immediately as the temperature of the raw materials reaches the eutectic temperature of the TiFe system. In the experiments, for *self-propagating combustion synthesis*, two-layered raw materials—Ti powders (heat source) as the upper layer and a mixture of Fe and Ti in the molar ratio of 1:1 as the lower layer—are used since reaction heat of TiFe production is small. One end of the sample is ignited, and the self-sustained combustion wave propagates to the other end. In this method, TiFe is formed as a product of the lower layer, but $TiH_2$ as formed as a byproduct of the upper layer. In conclusion, this mode of combustion synthesis is interesting from the viewpoint of the simultaneous production of TiFe and $TiH_2$. However, this is obviously not suitable for the mass production of TiFe, wherein only TiFe is to be produced. In contrast, the *self-ignition mode*[1] of combustion synthesis is more useful as compared to the self-propagation mode for improving the yield and saving excess Ti powder, which is used as the heat source. Therefore, the objective of this study is to investigate the *self-ignition combustion synthesis* (SICS) of TiFe, in which well-mixed powders of Ti and Fe in the molar ratio of 1:1 are uniformly heated under high-pressure hydrogen. In this study, mainly the hydrogenation of the product is examined. It should be noted that this method does not require the use of Ti as the heat source.

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[1] Some researchers refer to this mode as *thermal explosion*. However, few others prefer referring to this mode as self-ignition instead of thermal explosion because the word “explosion” sounds misleading. However, the phenomenon is the same.

0925-8388/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2009.02.008

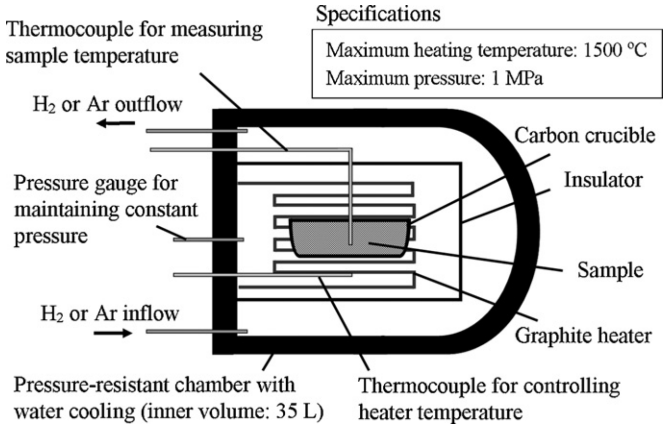

**Fig. 1.** Schematic diagram of SICS reactor.

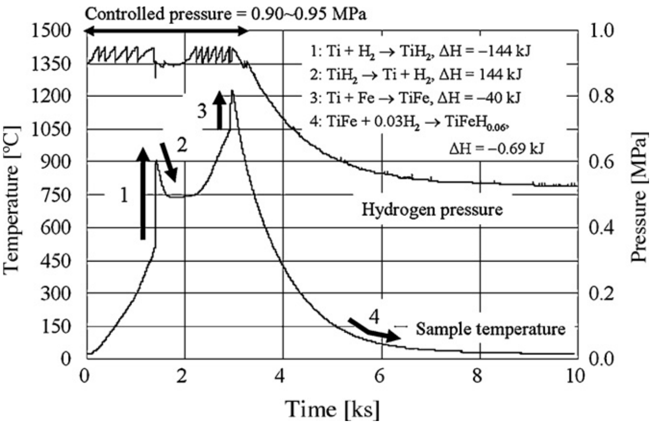

**Fig. 2.** Change in sample temperature and hydrogen pressure during SICS of TiFe.

Moreover, as compared to the $LaNi_5$-based alloys, TiFe synthesized by SICS is cheaper, does not require an activation process, and has a higher hydrogen storage capacity under similar working conditions.

## 2. Experimental

Fig. 1 shows the schematic diagram of the experimental apparatus, which has been previously used for the combustion synthesis of TiFe in the self-propagation mode (Saita et al. [14]). In this study, a graphite heater, which completely covered the sample, was used in order to carry out the combustion synthesis in the self-ignition mode, instead of the self-propagation mode. The device was used to heat the sample uniformly up to 1500 °C under high-pressure hydrogen up to 1.0 MPa because in SICS, the sample has to be preheated. The heating power, 2 kW, was sufficiently large for the uniform heating of the sample weighing 500 g at 1085 °C, the eutectic temperature of the TiFe system, at which the combustion synthesis of TiFe was initiated along with the evolution of reaction heat.

First, 500 g of the reagents (Kojundo Chemical Laboratory Co., Ltd.) Ti (99.9%, 45 μm pass) and Fe (99.9%, 3–5 μm) were mixed in the molar ratio of 1:1 in liquid acetone using a homogenizer at room temperature. Then, the mixture was kept in a desiccator in air for drying at 80 °C for 20 h. Next, the sample prepared was placed in a carbon crucible (80*W* mm × 150*L* mm × 45*H* mm), note that carbon does not contaminate TiFe [15], covered by a carbon sheet, as shown in Fig. 1. An R-type thermocouple placed inside a protective tube of alumina was introduced into the center of the sample. In the experiments, the furnace was evacuated to 20 Pa. Then up to 99.99999% pure hydrogen was charged to 0.9 MPa for combustion synthesis in the self-ignition mode after repeating the vacuuming and hydrogen charging processes four times. Then, the sample was uniformly heated to 1085 °C using the graphite heater. If the exothermic reaction was observed before reaching around 1085 °C at this time, the heating was stopped immediately and the sample was naturally cooled as preliminary test to identify formation phase. After uniformly heating to 1085 °C, the sample was naturally cooled in the same hydrogen atmosphere. Finally, the sample was removed from the furnace for various evaluations.

After the experiment, the product obtained was identified by X-ray diffraction (XRD) and observed under a scanning electron microscope (SEM). The hydrogenation property of the product was also evaluated using a pressure–composition–temperature measuring system (Suzuki Shokan Co., Ltd.) using Sieverts' method.

## 3. Results and discussion

Fig. 2 shows the change in the temperature at the center of the sample and the hydrogen pressure in the chamber during the SICS experiments. At around 500 °C, the first peak due to the exothermic reaction is observed, and then the sample temperature increases rapidly to 900 °C (see arrow 1). Note that the corresponding hydrogen pressure decreases instantly due to the hydrogen storage reaction. In the preliminary test, the sample was quenched shortly after the appearance of the first peak as shown in Fig. 2, for the XRD analysis. The XRD pattern has shown the product was a solid containing both titanium hydride and unreacted iron, but no TiFe. From the result, we assume that the first peak is caused by the following reversible reaction:

$$Ti + H_2 = TiH_2 + 144\,\mathrm{kJ} \tag{1}$$

Shortly after the appearance of the first peak, which has been attributed to the hydrogenation heat of titanium, the sample temperature decreases (see arrow 2) because thermodynamically, titanium hydride generated must be decomposed again to titanium and hydrogen at temperatures exceeding 930 °C. With the rapid increase in temperature to 1200 °C (see arrow 3), the second exothermic reaction is observed around 1085 °C, which is attributed to the evolution of heat due to the following TiFe reaction:

$$Ti + Fe = TiFe + 40\,\mathrm{kJ} \tag{2}$$

This temperature is slightly higher than the TiFe formation temperature, around 1085 °C, measured in the ignition mode [14]. It has been reported that the combustion synthesis of $Mg_2Ni$ initiates at the eutectic temperature, at which the formation of the liquid phase accelerates the reaction rate. On the basis of this fact, it can be easily predicted that the combustion synthesis of the TiFe starts around 1085 °C, the eutectic temperature of the Ti–Fe binary system (Fig. 3) [16], which explains why the TiFe formation reaction occurs at this temperature. However, during cooling, a significant increase in the temperature due to the hydriding reaction of titanium ($Ti + H_2 = TiH_2 + 144$ kJ) is not at all observed. Moreover, unreacted titanium has not been detected. The role of Eq. (1) is not clear, however we can easily predict that this treatment is important treatment from the similar technology. For example, it is well known that during the manufacture of magnets, exposure to hydrogen in the hydrogenation–disproportionation–decomposition–recombination (HDDR) cycle results in the formation of nanostructures and cracks in the magnets [17–19].

Fig. 4 shows the XRD patterns of the obtained product and commercially available TiFe (Kojundo Chemical Laboratory Co., Ltd.). There is no peak indicating the presence of impurities or unreacted raw materials; all the peaks of the product have been indexed to $TiFeH_{0.06}$, showing that the product has extremely high purity. Note that the peak corresponding to the product is at a slightly smaller angle as compared to that of commercially available TiFe. The results show that the second exothermic peak shown in Fig. 2 is caused by the formation of TiFe (Ti + Fe → TiFe + 40 kJ). Thus, TiFe is successfully synthesized by SICS.

From the results, it is clear that the hydriding process is complex. The steps involved in this process are as follows: (1) the reaction of titanium with hydrogen forming $TiH_2$ ($Ti + H_2 \rightarrow TiH_2$, $\Delta H = -144$ kJ, strongly exothermic) at around 500 °C; (2) the decomposition of $TiH_2$ to titanium and hydrogen ($TiH_2 \rightarrow Ti + H_2$,

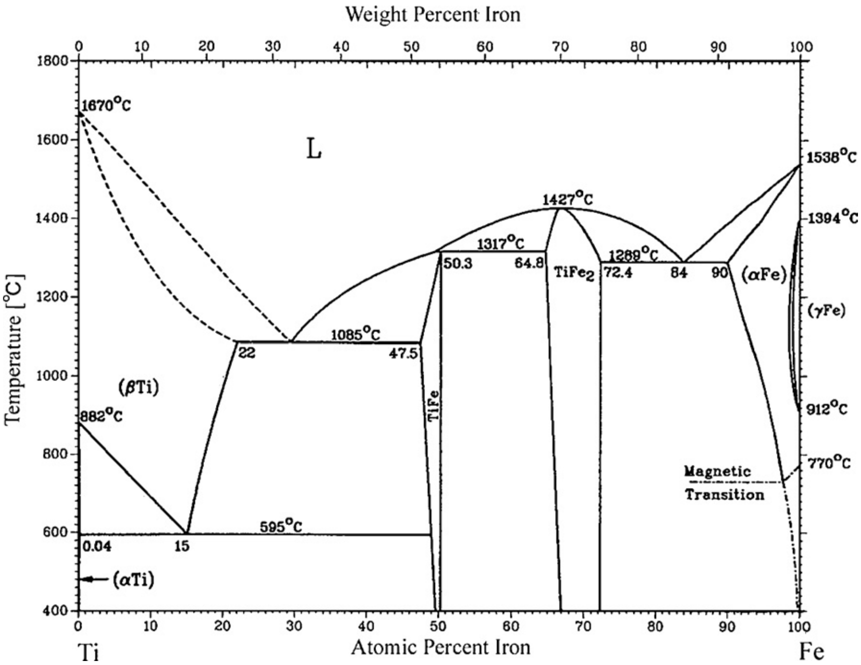

**Fig. 3.** Phase diagram of Ti–Fe binary system [16].

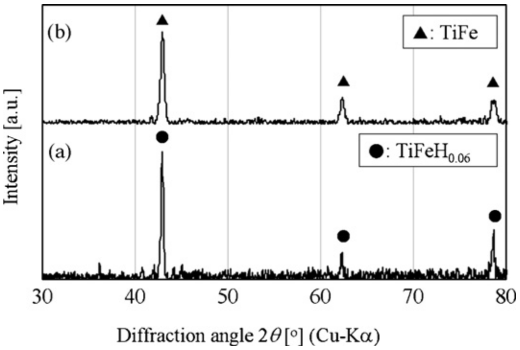

**Fig. 4.** XRD patterns of (a) TiFe synthesized by SICS and (b) commercially available TiFe.

$\Delta H$ = +144 kJ, strongly endothermic) at around 930 °C; (3) the synthesis of TiFe (Ti + Fe → TiFe, $\Delta H = -40$ kJ, exothermic) at around 1085 °C; and (4) the reaction of TiFe with hydrogen forming $TiFeH_{0.06}$ ($TiFe + 0.03H_2 \rightarrow TiFeH_{0.06}$, slightly exothermic) at around room temperature.

According to the pressure–composition isotherm, TiFe formed at high temperature and then is hydrogenated very quickly near room temperature during the cooling process of SICS, because its surface is not exposed to air and not oxidized.

Fig. 5 shows the SEM images of titanium (99.9%, 45 μm pass) and iron (99.9%, 3–5 μm) powders (A), the product obtained by SICS (B), and commercially available TiFe powder (C). The product of SICSed TiFe is a weak agglomerate because during SICS, the ignition takes place at a temperature lower than the melting point. It has been revealed that the formation of the eutectic composition (partial liquid phase) of Ti and Fe accelerates the reaction rate drastically. Furthermore, since the obtained product is considerably more porous as compared to the commercially available product, the former can be easily pulverized and has sufficiently high reaction rate.

Fig. 6 shows the initial hydriding curves of the obtained product with particle size in the range of 0.5–1.0 mm and the commercially available product at 25 °C. Both the samples have been compressed under hydrogen at 4 MPa without employing an activation process after the vacuum treatment for 3 h by turbo-molecular pump. The commercially available product is not hydrogenated, as reported

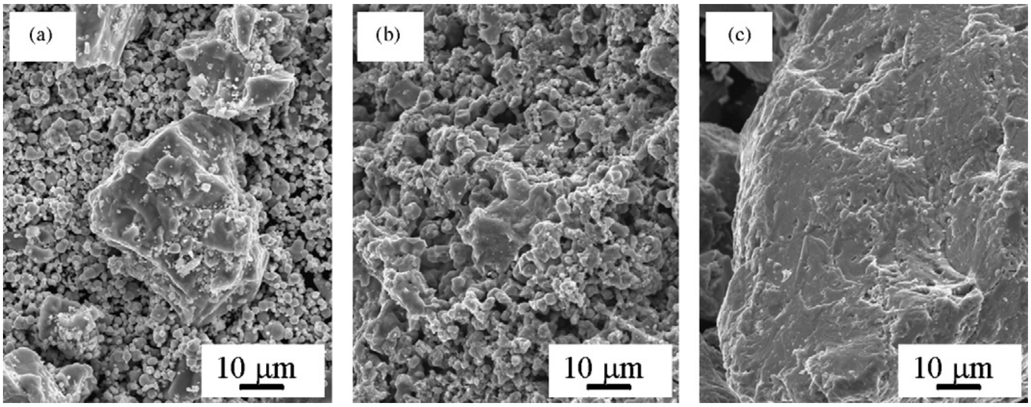

**Fig. 5.** SEM images of (a) raw material, (b) TiFe synthesized by SICS, and (c) commercially available TiFe.

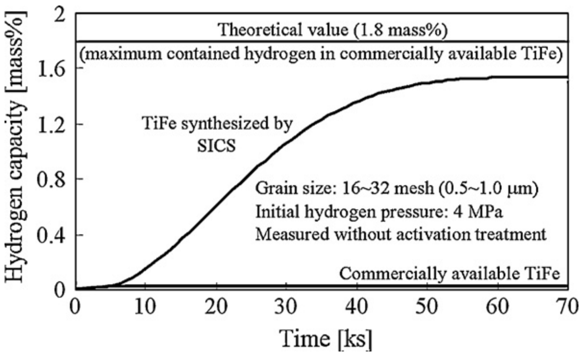

**Fig. 6.** Initial hydriding curves for TiFe obtained by SICS and commercially available TiFe at 25 °C.

previously [2,3]. In contrast, the product stores hydrogen immediately after the compression, and the equilibrium content of hydrogen reaches 1.55 mass% in 60 ks. This amount is same as that in a product obtained by using the arc melting method [2]. It should be noted that the amount of contained hydrogen will increase to 1.8 mass% at higher pressure. Most significantly, the product does not require any activation process. In fact, the conventional products obtained by ingot metallurgy require the activation processes to be repeated around 10 times.

The initial activity of TiFe improved drastically by SICS because the product synthesized by SICS contains hydrogen slightly such as $TiFeH_{0.06}$, and not a TiFe alloy. That is, the product releases hydrogen during the vacuuming process before hydrogenation. The surface of product, which gets contaminated on exposure to air, develops cracks due to the hydrogen release, and the high activity interface is exposed. The hydrogenation of the product followed from there in the hydrogen atmosphere.

In conclusion, the results show that SICS is very effective for improving the initial activity of TiFe. However, the final product $TiFeH_2$ is not obtained at room temperature. It is because when the product is removed from the furnace, the contained hydrogen is released due to the decrease in the partial pressure of hydrogen even if the product is full hydride. Otherwise, the retention time of the product in the furnace for hydriding was too short. The SICS using the furnace cannot be applied in order to obtain a full hydride of TiFe. In order to obtain a high-concentration TiFe hydride, it is important to modify the furnace.

## 4. Conclusion

SICS has been used to produce TiFe, in which well-mixed powders of Ti and Fe are heated to 1085 °C under high-pressure hydrogen at 1 MPa, and then heating was stopped the moment the exothermic reaction takes place, in order to maintain the energy to be constant. The conclusions are as follows:

(1) Pure $TiFeH_{0.06}$ phase has been successfully obtained through the following four continuous steps:
   (i) *First ignition* ($T \approx 500\,^\circ C$): $Ti + H_2 \rightarrow TiH_2$, $\Delta H = -144$ kJ
   (ii) *Decomposition* ($T \approx 900\,^\circ C$) of $TiH_2$: $TiH_2 \rightarrow Ti + H_2$, $\Delta H = 144$ kJ
   (iii) *Second ignition* ($T \approx 1085\,^\circ C$): $Ti + Fe \rightarrow TiFe$, $\Delta H = -40$ kJ
   (iv) *Hydrogenation* at low temperature: $TiFe + 0.03H_2 \rightarrow TiFeH_{0.06}$, $\Delta H < 0$ kJ

   Here, 1085 °C is the eutectic temperature of the TiFe system. Steps (i) and (ii) are regarded as important steps in the synthesis process.
(2) As compared to the conventional products obtained by ingot metallurgy, TiFe synthesized by SICS can store hydrogen more quickly and does not require an activation process.
(3) TiFe obtained is highly porous and not dense. This explains why the products synthesized by SICS have improved reaction rate of hydrogenation and dehydrogenation efficiently.

The results also show that SICS can be used for the mass production of TiFe since it saves time and energy, has excellent kinetics, and yields a high-purity product.

## Acknowledgements

This research was partly supported by the Ministry of the Environment, Japan, under the projects “Demonstration of Green Hydrogen-based Community in Honjo-Waseda area” and “Development of Hydrogen Freezer Using Industrial Waste Heat or Solar Heat for Reducing $CO_2$ Emission.”

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