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Hydriding combustion synthesis of TiFe

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Abstract

Titanium iron (TiFe) is one of the most attractive metal hydrides because of abundant and low cost raw materials and moderate conditions for hydrogenation and dehydrogenation; however, it has not been practically used due to time-consuming and energy-consuming activation treatment. Aiming to improve the initial activity of TiFe, we applied hydriding combustion synthesis (HCS), which has attractive advantages for the direct production of metal hydride; time saving, energy saving, and highly pure product that is highly hydrogenated and does not require the activation treatments for metal hydride production, to the TiFe production. In the experiments, hydrogen storage reaction of titanium ($Ti + H_2 = TiH_2 + 144$ KJ) was utilized for HCS of TiFe because the adiabatic flame temperature of this reaction was estimated to be 2000 °C, which is enough high for melting both iron and titanium. The raw material of Ti and Fe powders mixed with 1:1 molar ratio was covered with additional Ti powders from above and placed in hydrogen atmosphere. After the Ti powders were ignited by electrically heated carbon filament, the TiFe synthesis reaction ($Ti + Fe = TiFe + 40$ kJ) occurred successfully. The HCSed TiFe was activated easily and stored hydrogen approximately 1.7 mass% indicating improved initial activity for hydrogen storage.

Keywords: Metal hydrides; Gas–solid reaction; Powder metallurgy; Thermal analysis

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1. Introduction

Titanium iron (TiFe) is one of the most attractive metal hydrides because of abundance and low cost of raw materials and moderate conditions for hydrogenation and dehydrogenation; however, TiFe stores only small amounts of hydrogen without activation treatment, which requires a temperature over 400 °C and repeating hydrogen charging and discharging some times, because its surface is easily poisoned in air and is prevented from hydriding. Difficulties with activation make TiFe to remain unpractical in spite of the practical features. Osumi et al. quantified the problem evaluating various metal hydrides in terms of their hydrogen storage properties including activation ease, hydrogen capacity, cycling property, heat of formation, temperature and pressure required for hydriding reaction, production cost and safety [1,2]. In the evaluation, TiFe scored 25 points as much as the points of $LaNi_5$, which has been used practically as the electrode in Ni–MH battery [3,4]. If the activation ease of TiFe was better, the material's overall desirability would have been evaluated superior to $LaNi_5$ system metal hydrides; that is, its activation hardness prevents TiFe from being popularized in spite of its other sufficient hydrogen storage abilities.

Therefore, it is worthwhile to alleviate the activation difficulty of TiFe. We examined HCS, which successfully synthesized highly pure metal hydride without activation treatment in previous studies [5,6], in TiFe production without activation treatment. The HCS is expected to be applicable to TiFe because the hydrogenation of Ti has been reported to be self-propagating [7] with a very large heat of formation.

$$Ti + H_2 = TiH_2 + 144\,\text{kJ} \qquad (1)$$

The adiabatic flame temperature, T_{ad}, of the reaction is estimated to be as high as 1800 °C. Even if equimolar Fe were added to Ti, the T_{ad} is estimated to be as high as 1600 °C, which is higher than the eutectic temperature of the Ti–Fe system. A previous study showed that the HCS is accomplished when the raw

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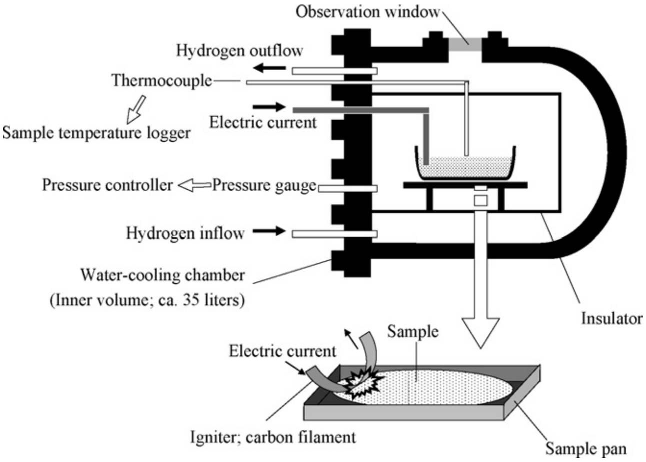

Fig. 1. Schematic diagram of HCS reactor.

materials are heated to the eutectic temperature of the system [8]; therefore, it seems to be possible to synthesize TiFe, whose eutectic temperature is 1085 °C, by HCS utilizing the large reaction heat of TiH_2 formation. For those reason, the HCS of TiFe metal hydride was examined by using an HCS apparatus that was newly developed with an ignition function.

2. Experimental

Fig. 1 is a schematic diagram of an experimental apparatus that was newly developed to ignite HCS reaction in a hydrogen atmosphere. The igniter was made of a carbon filament. When electricity is applied, the filament generates Joule heat and partially heats a sample, thereby causing ignition. The ignition can be performed safely because the atmosphere in the reactor can be evacuated and substituted with highly pure hydrogen, which is not explosive without oxygen. The reactor has four thermocouples inside and an observation window above the sample. Consequently, the propagation behavior of HCS can be monitored thermodynamically and visually. The pressure inside the reactor can be controlled using the On–Off controller.

To verify safety of ignition in a hydrogen atmosphere, Ti powder (99.9%, 45 μm pass) was preliminary ignited in hydrogen atmosphere that was set initially at 0.9 MPa. Thereafter, hydrogen pressure was not controlled because the reactor was closed to observe the pressure change and to prepare for eventuality of explosion. Result of visual observation was shown in Fig. 2. The photos showed an exemplar of combustion synthesis: The igniter partially heated the Ti (Fig. 2(a)) and that the Ti subsequently produced red light (Fig. 2(b)). The light propagated from around the igniter to the entire sample (Fig. 2(c)); that is, combustion synthesis successfully propagated and completed. The temperature and pressure changes during the combustion are shown in Fig. 3. The temperature of Ti was increased rapidly after ignition, and the hydrogen pressure was decreased gradually throughout the reaction. The X-ray diffraction (XRD) pattern of the product was identified with TiH_2. Those results demonstrated that the exothermic reaction described in Eq. (1) had occurred and had propagated safely as a combustion wave. After it increased to maximum, the sample temperature decreased slowly. The temperature drop was maintained at a temperature of approximately 700 °C, which was equal to the hydrogen storage temperature of Ti. This result checked with the previous report on combustion synthesis of TiH_2, in which Ti was first hydrided rapidly but later dehydrided due to the overly high temperature of the combustion wave, then hydrided again while the mass was cooled slowly [7]. The maximum temperature during the combustion synthesis of TiH_2 was approximately 900 °C, which was slightly lower than expected. The difference between observed temperature and calculated adiabatic flame temperature was because of heat loss and/or endothermic reaction of TiH_2 deformation; therefore, in the experiments, excess Ti was added to the samples to supply heat and to increase the temperature more.

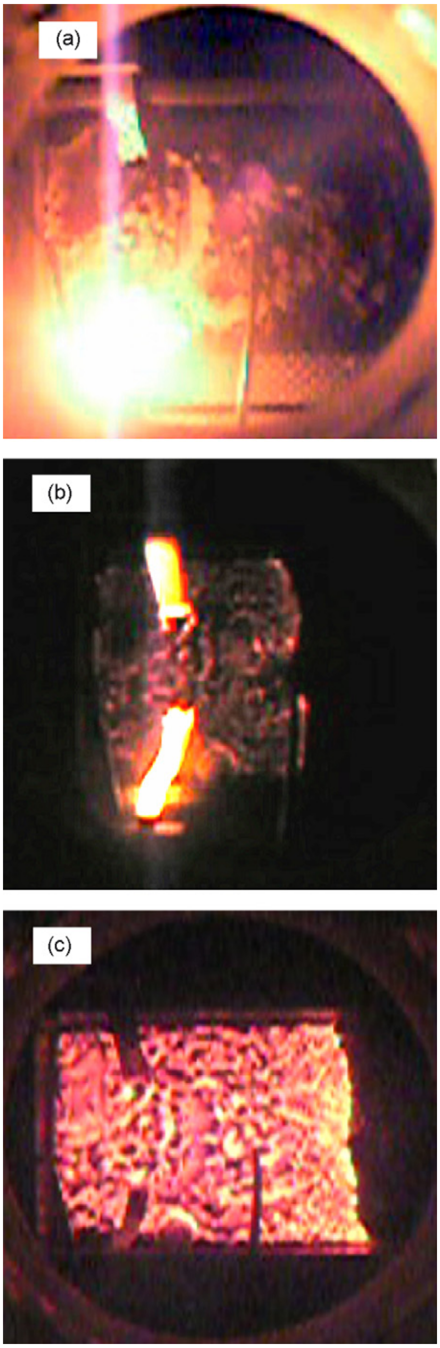

Fig. 2. Visual observation of combustion synthesis of TiH_2 (a) igniter was partially heating Ti, (b) light of combustion wave was propagating from the left to right and (c) finally propagated entire sample.

Four samples were prepared from Ti powders (99.9%, 45 μm pass) and Fe powders (99.9%, 3–5 μm). Three samples were 200 g of the mixtures of $Ti + xFe$ with $x = 1$, 0.5, 0.25. The remaining sample was 200 g of equimolar mixture of Ti + Fe and additional 100 g of Ti, which covered the mixture. Each sample was set in the reactor and ignited in a hydrogen atmosphere of 0.9 MPa. The pressure was controlled as constant. Ignition was monitored through the observation window. The products were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The hydrogenation behavior of the product was measured using a pressure-composition-isotherm measurement apparatus (Suzuki Shokan Co., Ltd.).

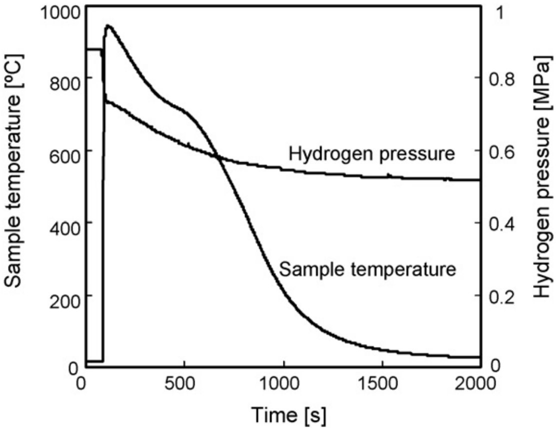

Fig. 3. Changes of sample temperature and hydrogen pressure during combustion synthesis of TiH_2.

3. Results and discussion

As the results, two samples with molar mixing ratios of Ti:Fe = 1:1, 0.5 produced no reaction. The sample of Ti:Fe = 1:0.25 showed a light that propagated slightly, but it did not propagate even 1 cm. The results indicated that the heat of TiH_2 formation was discharged and insufficient to propagate to the sample even though more than three times the equimolar amount of Ti was added.

In the sample of Ti + Fe covered with additional Ti layer, a combustion wave was observed propagating throughout the Ti layer. The XRD pattern of the product in Ti + Fe layer is shown in Fig. 4. There was no peak of impurities or raw materials. All the peaks were indexed with $TiFeH_{0.06}$, which were slightly shifted from the peaks of TiFe to small angles, revealing that the HCS successfully produced hydride of TiFe. Although the amount of layered Ti was almost as great as Ti in the lower layer, the method to supply heat by the excess Ti layer was more effective than uniformly mixing Fe with three times excess of Ti as described above.

The temperature changes during HCS were measured using a thermocouple inserted into the layer of Ti + Fe. The changes are shown in Fig. 5. The sample temperature increased rapidly to 1044 °C indicating that the combustion wave had propagated in the Ti + Fe layer. The temperature after the combustion waves was cooled slowly, and stopped for a while at approximately 700 °C for re-hydriding of Ti that dehydrided at the overly high temperature for hydride within the combustion wave, as in the preliminary experiment described in Fig. 3. The maximum temperature was almost equal to the eutectic temperature of Ti–Fe system, above which the HCS was expected to occur. Because the combustion wave of TiH_2 formation was observed and TiFe was synthesized, there must have been at least two combustion waves due to the exothermic phenomena from TiH_2 formation in cover layer and TiFe formation in sample layer. Actually, an enlarged figure of the temperature changes (Fig. 5(b)) showed multiple step of temperature increase. Note that the step was not double, but triple: first, temperature increased quickly over 400 °C, indicating the first combustion wave. Thereafter, the rate of temperature increase decreased gradually until the temperature increased to 500 °C. At around 500 °C, the rate of temperature increase regenerated and the temperature increased to 800 °C more rapidly than in the first combustion wave. The pattern indicated the second combustion wave. The temperature increase slowed suddenly over 800 °C. Finally, the temperature increase was regenerated again as the third combustion wave.

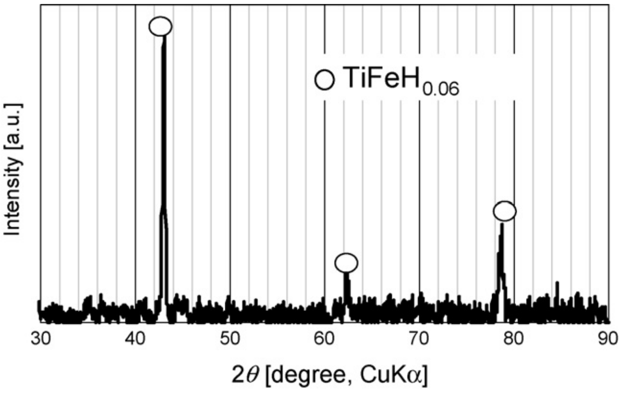

Fig. 4. XRD pattern of the product.

The first combustion wave accompanied the combustion wave in the upper Ti layer. Therefore, its cause was the heat of TiH_2 formation in the upper layer. The latter two waves were considered to be in the lower Ti + Fe layer. The possibility exists of two combustion waves in the Ti + Fe layer: TiH_2 formation and TiFe synthesis. TiFe synthesis was described in Eq. (2):

$$\mathrm{Ti} + \mathrm{Fe} = \mathrm{TiFe} + 40\,\mathrm{kJ} \quad (2)$$

The formation heat of TiFe was as much as one-third of that of TiH_2, which indicated that the temperature increase caused by the TiFe formation should be smaller than that for TiH_2 formation. The temperature increase in the third combustion wave was smaller than in the second one. Therefore, the second wave was considered to be attributable to TiH_2 formation and the third wave was caused by TiFe formation. In addition, the second temperature increase was ceased at 800 °C, where the Gibbs's energy change of TiH_2 formation becomes negative. The second combustion wave was likely to represent TiH_2 formation, which was reduced drastically by the reverse reaction of TiH_2 deformation over 800 °C. Though another endothermic reaction described in Eq. (3) was also possible at a temperature over 600 °C, it was not determined in the temperature change; therefore, the discontinuity of temperature change around 800 °C was regarded as the TiH_2 deformation. The propagation of three combustion waves in the sample is summarized in Fig. 6.

$$\mathrm{TiH_2} + \mathrm{Fe} = \mathrm{TiFe} + \mathrm{H_2(g)} - 104\,\mathrm{kJ} \quad (3)$$

Fig. 7 shows the SEM observations of the raw material and the product. The raw material included Ti powders (<45 μm) and Fe powders (3–5 μm) as prepared. Mass of the product was porous, and the surface was smooth. There was no particles as in the raw material. The result revealed that all the particles of raw materials had melted. The liquid generation during HCS enabled liquid-liquid reaction between Ti and Fe and thereby enhanced the alloying reaction.

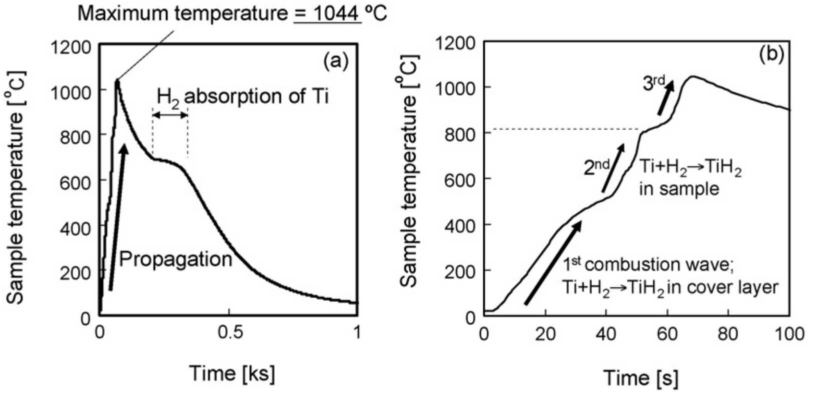

Fig. 5. Temperature change during the HCS (a) and enlarged one (b).

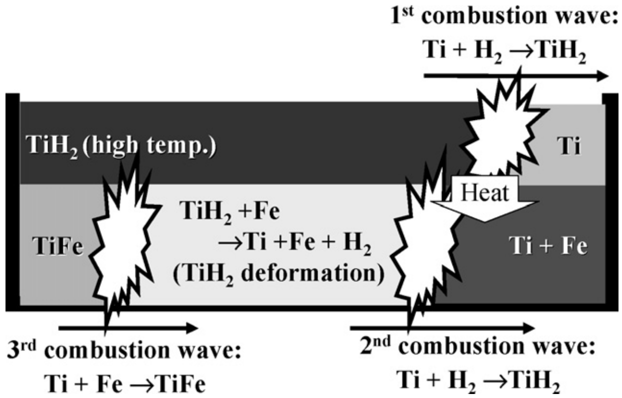

Fig. 6. Schematic diagram of reaction mechanism of HCS of TiFe (three combustion waves in the HCS).

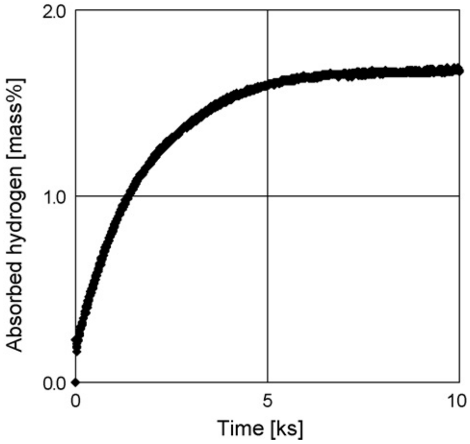

Fig. 8. Hydrogenation behavior of the product at 25 °C.

Fig. 8 shows the hydrogenation behavior of the product at 25 °C. It is noteworthy that the product required an activation treatment. The activation treatment was done by evacuating the product and charging hydrogen on the product at a temperature of 400 °C; then, the product was cooled to 25 °C. After the activation treatment, the product stored hydrogen as much as 1.7 mass%; that is equal to 95% of reported hydrogen capacity of TiFe. The activation difficulty was drastically improved.

In comparison to the previous study on HCS, which indicated that the product obtained by HCS required no activation treatment, the results in this study showed that HCS did not completely alleviated the activation difficulty of TiFe; that is, because the hydrogen in the HCS product was greatly advantageous for reducing activation treatment, the product could not take the advantages of HCS while it was not the β-hydride, but only the β-hydride of TiFe as shown in Fig. 4. Further improvements of the reactor, such as attaching a cooling system or pressurizing hydrogen atmosphere, would be effective to hydrogenate the product within the single operation of HCS, to increase the hydrogen density in the product, and to improve the initial activity of TiFe untill it stores hydrogen without activation treatment.

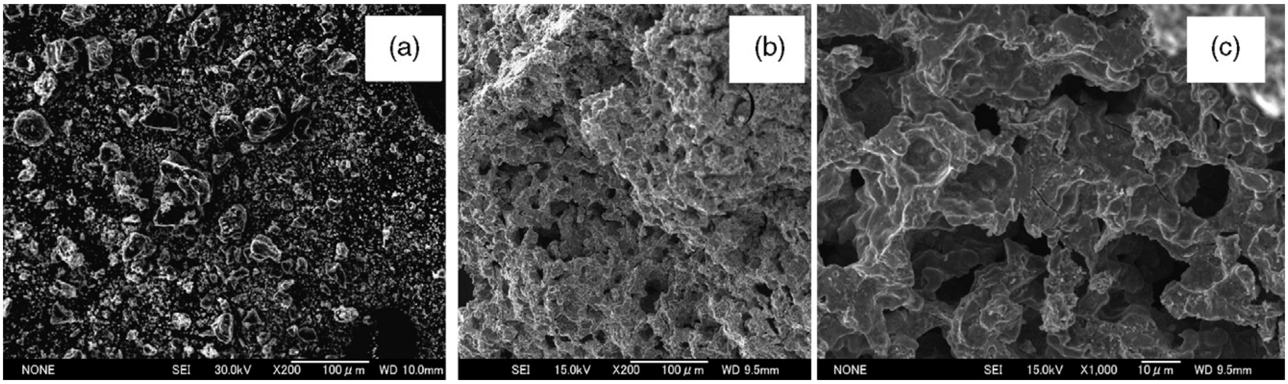

Fig. 7. SEM images of the raw material (a) and the product (b and c). (a) Powders of Ti and Fe mixed with 1:1 molar ratio. (b and c) As-synthesized product of TiFe.

4. Conclusion

To produce TiFe hydride and to improve the initial activity of TiFe, HCS was proposed. Its feasibility was investigated theoretically and examined using an HCS apparatus that was newly developed to enable ignition in a hydrogen atmosphere.

With excess Ti as a heat supply, HCS produced α-hydride of TiFe. Although the product required an activation treatment once, the activation time was shortened drastically and the product was activated up to 95% of maximum capacity, revealing that the initial activity was greatly improved in comparison to that of conventional product.

The results indicated that room for improvement exists in synthesis conditions to obtain activation-free TiFe taking the advantages of HCS.

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References

[1] T. Osumi, H. Suzuki, A. Kato, K. Oguro, M. Nakane, J. Less-Common Metals 74 (1980) 271–277.

[2] Y. Osumi, Metal Hydride—its Property and Application, Enlarged Edition, Kagaku-Kogyo-Sya, Sec. 8.11, 1986, pp. 192–197.

[3] F.G. Will, Hermetically sealed secondary battery with lanthanum nickel anode, US patent 3874958 (1975).

[4] A. Percheron-Guegan, J.C. Achard, J. Sarradin, G. Bronoël, Alliages à base de Lanthane et de Nickel et leurs applications électrochimiques, French patent 7516160 (1975).

[5] I. Saita, L. Li, K. Saito, T. Akiyama, Mater. Trans. 43 (2002) 1100–1104.

[6] I. Saita, K. Saito, T. Akiyama, J. Alloys Compd. 390 (2005) 265–269.

[7] A.A. Zenin, G.A. Nersisyan, M.D. Nersesyan, Combust. Explos. Shock Waves, USSR 18 (1982) 444–450.

[8] L. Li, T. Akiyama, J. Yagi, Intermetallics 7 (1999) 671–677.