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Self-ignition Combustion Synthesis of TiFe in Hydrogen Atmosphere

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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 are uniformly heated up to 1085 °C, the eutectic temperature of Ti-Fe binary system, in a pressurized hydrogen atmosphere at 1.0 MPa. The electric source is disconnected immediately after the ignition between Ti and Fe, and the mixture is cooled naturally. In the experiments, the exothermic reaction $\text{Ti} + \text{Fe} \rightarrow \text{TiFe} + 40 \text{ kJ}$ occurs at 1085 °C after the hydrogenation and decomposition of Ti. X-ray diffraction analysis shows that the final product has only one phase— $\text{TiFeH}_{0.06}$ —which contains 1.55 mass% of hydrogen at 4.0 MPa of hydrogen pressure. The product obtained by SICS contains 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 is observed using a scanning electron microscope. In conclusion, the SICS of TiFe saves time and energy, yields products with high porosity and small crystals, enables easy hydrogenation, and does not require activation processes.

Keywords: Hydrogen storage materials; Powder metallurgy; Gas-solid reactions

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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 *hydriding combustion synthesis (HCS)* techniques [4–33] have been reported; in these 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 [1] 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 TiH₂. 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 hydride, 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.

Moreover, as compared to the LaNi₅-based alloys, TiFe hydride synthesized by SICS is cheaper, does not require an activation process, and has a higher hydrogen

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.

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. [4]). In this study, a graphite heater, which completely covers the sample, is used in order to carry out the combustion synthesis in the self-ignition mode, instead of the self-propagation mode. The device is 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, is 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 is 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 [34] (80W $\times$ 150L $\times$ 45H mm) 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 4 times. Then, the sample was uniformly heated to 1085 °C using the graphite heater, after which the sample was naturally cooled in the same hydrogen atmosphere.

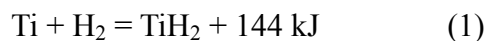
Finally, the sample was removed from the furnace for various evaluations.

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 gets 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 is 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.



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 [1]. 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.



This temperature is slightly higher than the TiFe formation temperature, around 1085 °C, measured in the ignition mode [1]. It has been reported that the combustion synthesis of Mg₂Ni 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), 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 ($\text{Ti} + \text{H}_2 = \text{TiH}_2 + 144 \text{ kJ}$) 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 [36-38].

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 $\text{TiFeH}_{0.06}$, 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 ($\text{Ti} + \text{Fe} \rightarrow \text{TiFe} + 40 \text{ kJ}$). Thus, TiFe hydride 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 hydride ($\text{Ti} + \text{H}_2 \rightarrow \text{TiH}_2$, $\Delta H = -144 \text{ kJ}$, strongly exothermic) at around 500°C ; (2) the decomposition of TiH_2 to titanium and hydrogen ($\text{TiH}_2 \rightarrow \text{Ti} + \text{H}_2$, $\Delta H = +144 \text{ kJ}$, strongly endothermic) at around 930°C ; (3) the synthesis of TiFe ($\text{Ti} + \text{Fe} \rightarrow \text{TiFe}$, $\Delta H = -40 \text{ kJ}$, exothermic) at around 1085°C ; and (4) the reaction of TiFe with hydrogen forming $\text{TiFeH}_{0.06}$ ($\text{TiFe} + 0.03\text{H}_2 \rightarrow \text{TiFeH}_{0.06}$, 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 synthesized by SICS 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 previously [2,3]. In contrast, the product contains 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 [3]. 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 is a hydride, and not an 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 hydride, in which well-mixed powders of Ti and Fe are heated to 1085 °C under high-pressure hydrogen at 1 MPa, and then heating is stopped the moment the exothermic reaction takes place, in order to maintain the energy to be constant. The conclusions are as follows:

1) Pure TiFe hydride has been successfully obtained through the following four continuous steps:

i) *1st ignition* ($T \approx 500\text{ °C}$): $\text{Ti} + \text{H}_2 \rightarrow \text{TiH}_2$, $\Delta H = -144\text{ kJ}$

ii) *Decomposition* ($T \approx 900\text{ °C}$) of TiH_2 : $\text{TiH}_2 \rightarrow \text{Ti} + \text{H}_2$, $\Delta H = 144\text{ kJ}$

iii) *2nd ignition* ($T \approx 1085\text{ °C}$): $\text{Ti} + \text{Fe} \rightarrow \text{TiFe}$, $\Delta H = -40\text{ kJ}$

iv) *Hydrogenation* at low temperature: $\text{TiFe} + 0.03\text{H}_2 \rightarrow \text{TiFeH}_{0.06}$, $\Delta H < 0\text{ kJ}$

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 contains 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.

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Tables and figure legends

Fig. 1. Schematic diagram of SICS reactor.

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

Fig. 3. Phase diagram of Ti-Fe binary system [35].

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

TiFe.

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.

*** Prime Novelty Statement**

Prime novelty of this study is new synthesis method of hydrogen storage alloy of titanium iron and its hydrogenation property of the product. The method is combustion synthesis of uniform heating type (self-ignition type); we named this method self-ignition combustion synthesis (SICS). As compared to the conventional products obtained by ingot metallurgy, TiFe synthesized by SICS contains hydrogen more quickly and does not require an activation process.

Figure 1
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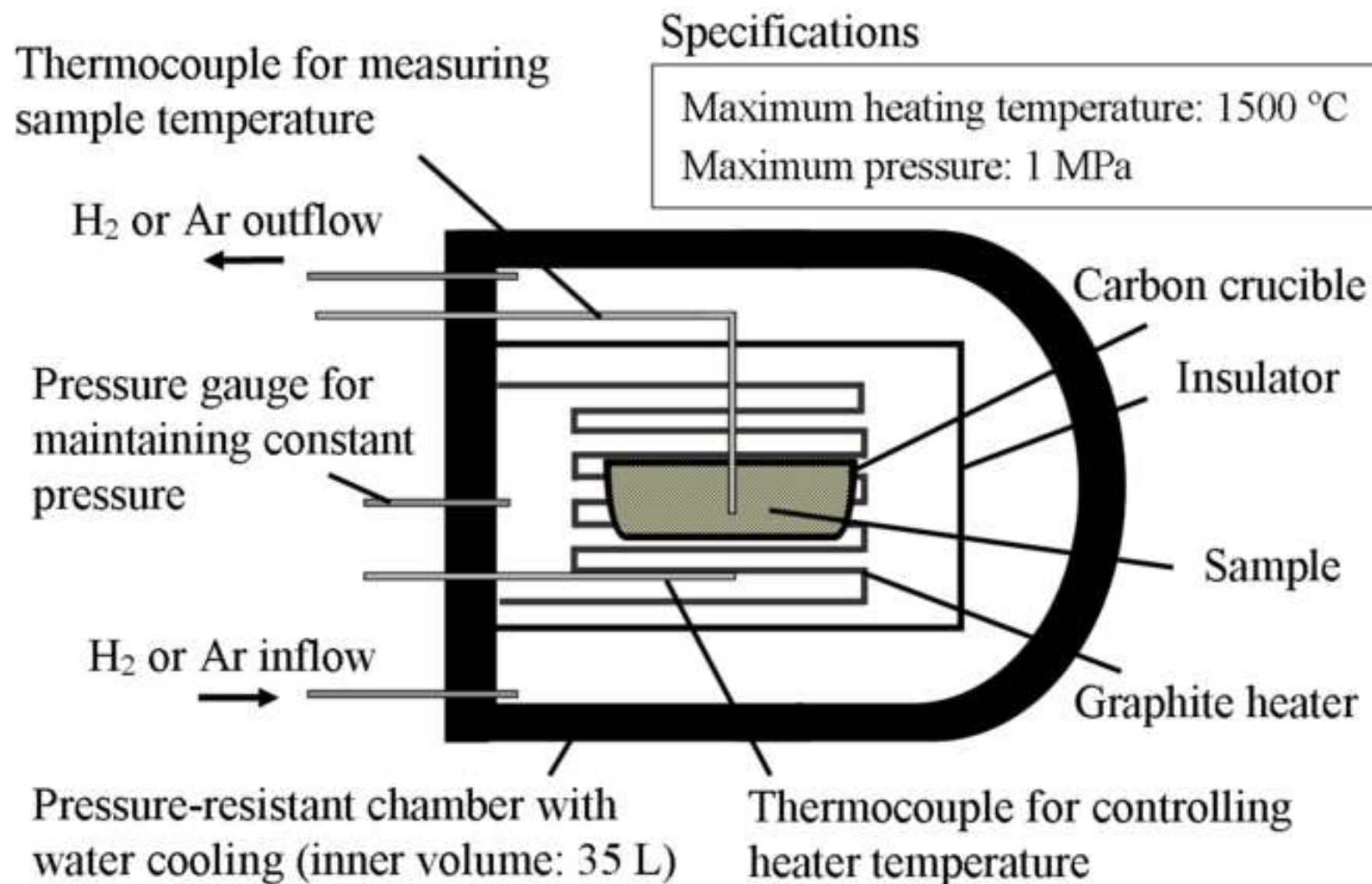


Figure 2
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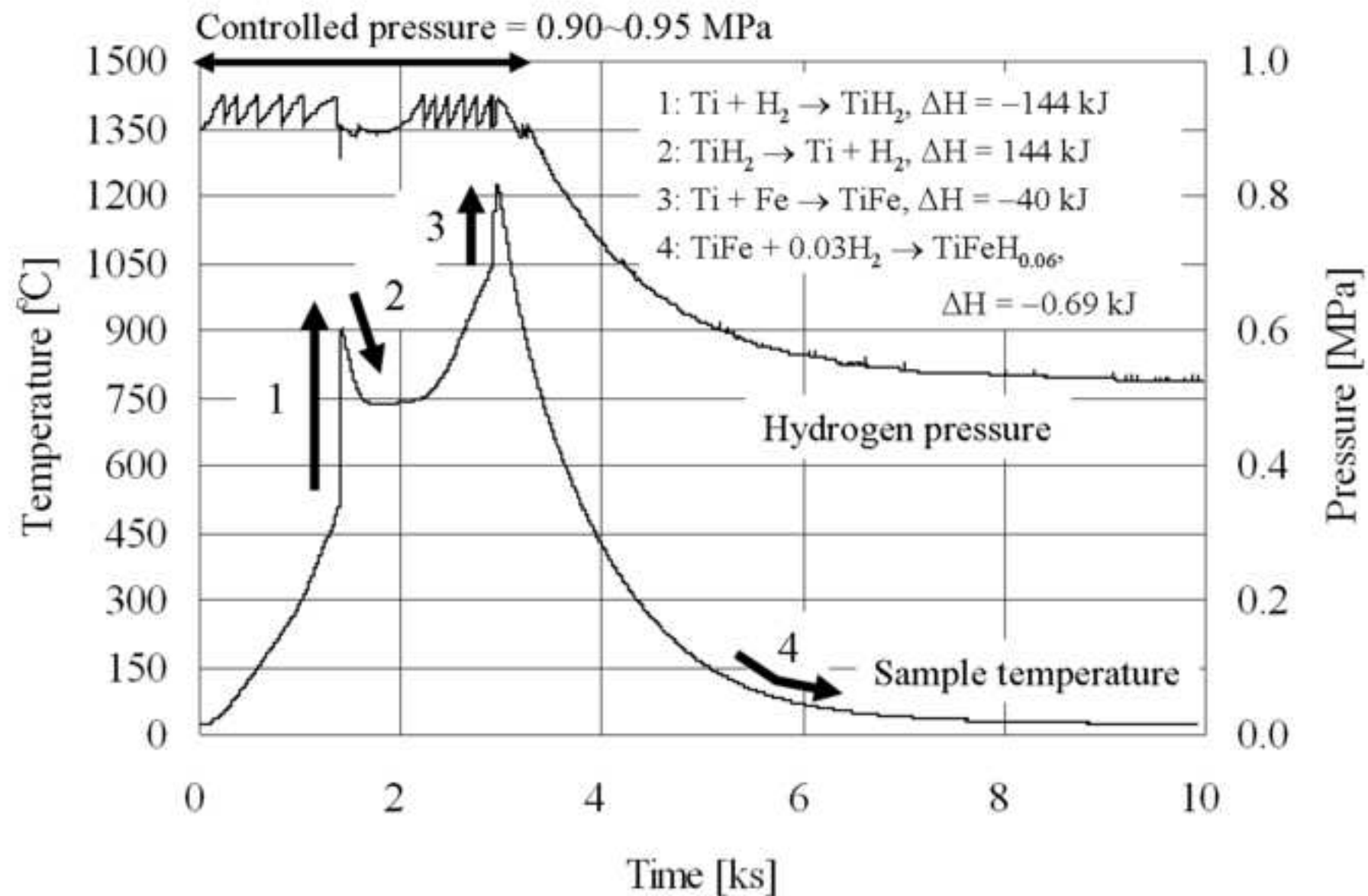


Figure 3
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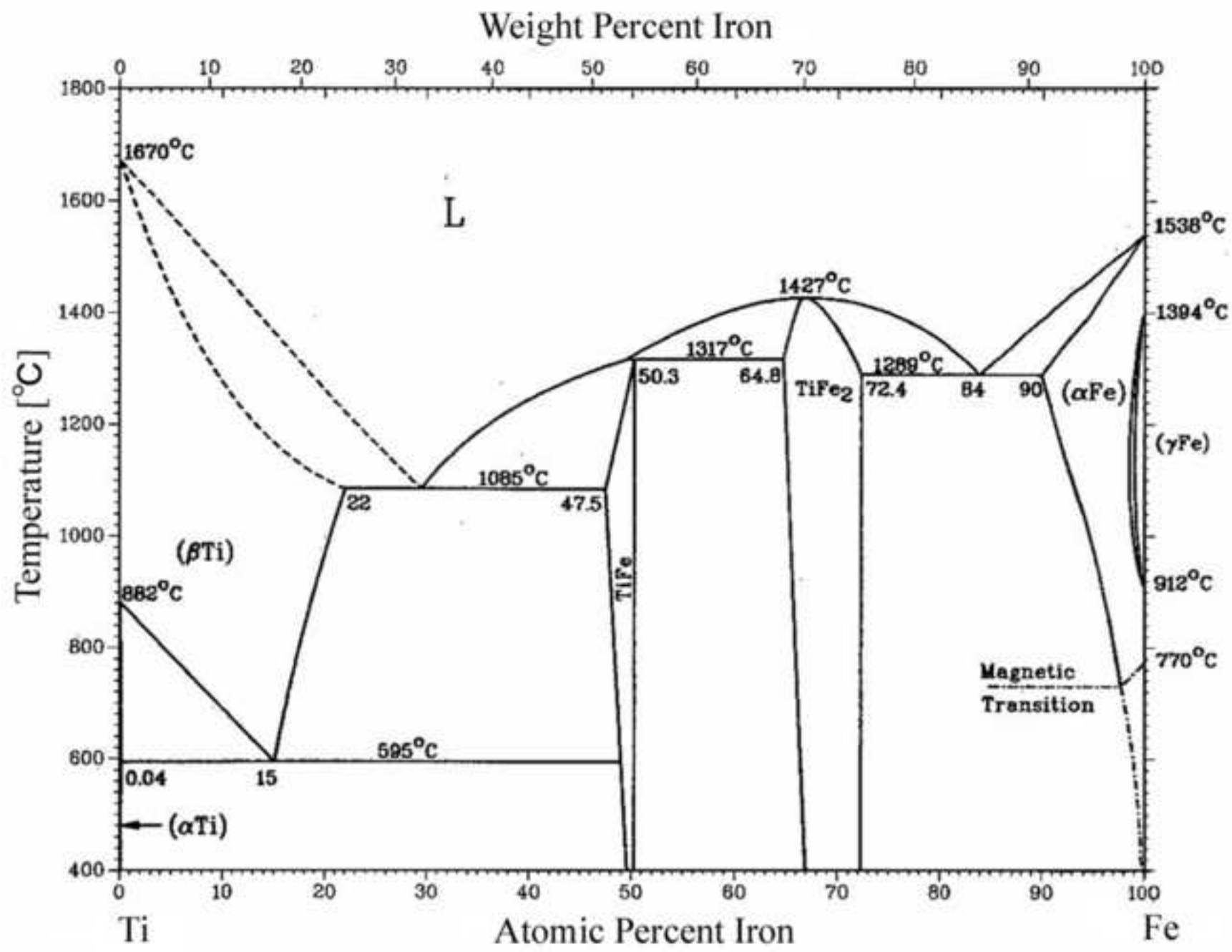


Figure 4
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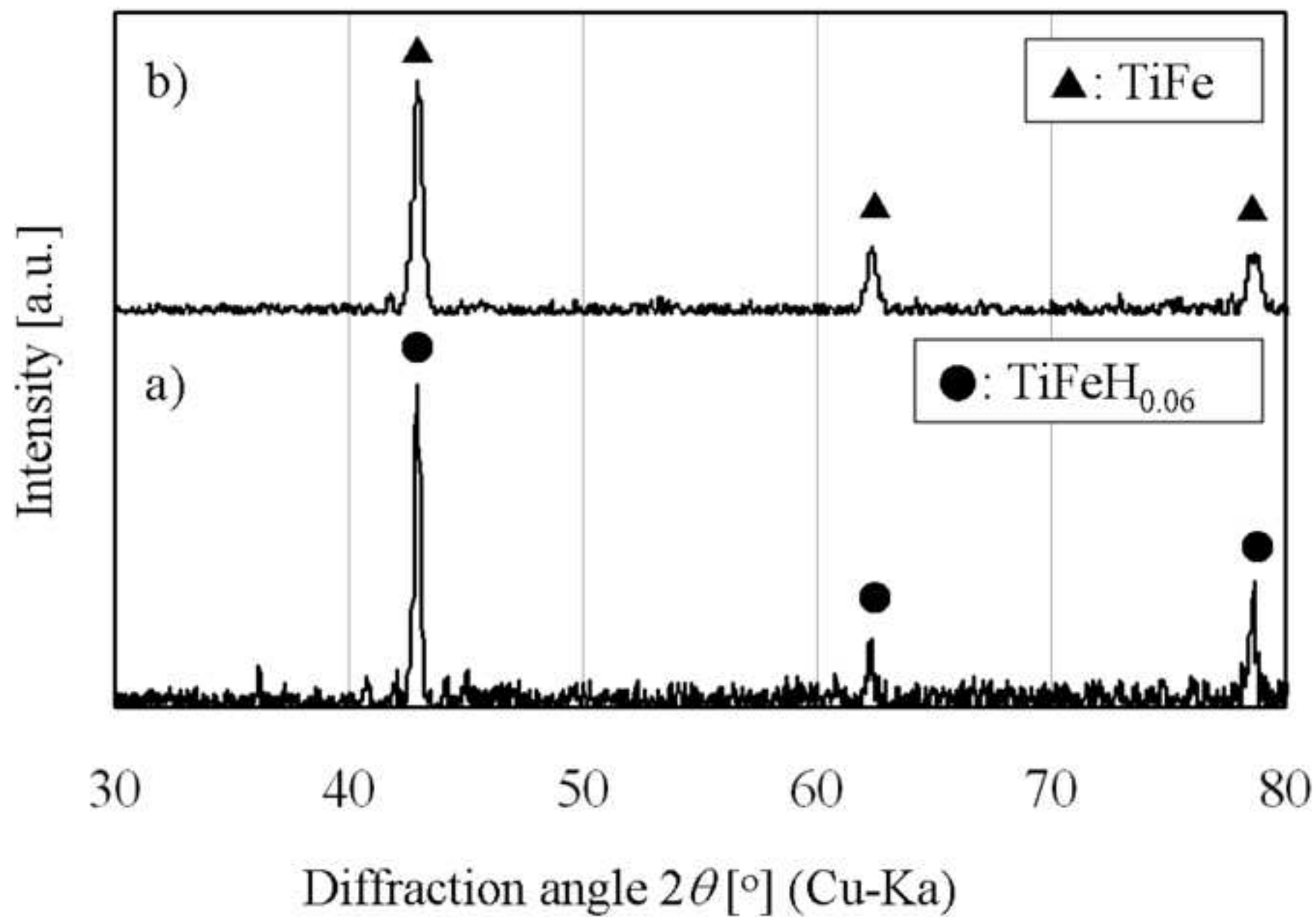


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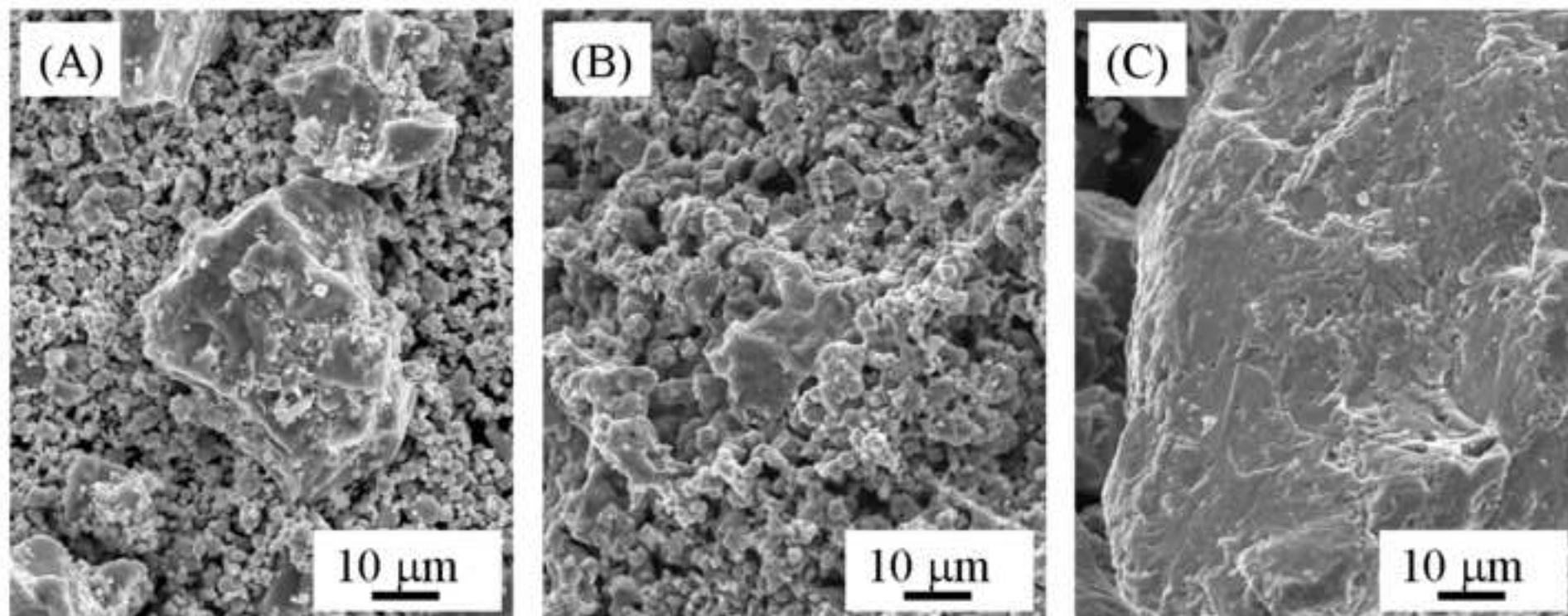


Figure 6
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