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# A comparison of $\text{TiF}_3$ and $\text{NbF}_5$ catalytic effects on hydrogen absorption and desorption kinetics of a ball-milled $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$ alloy

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In this investigation, the as-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) composites were successfully produced via ball milling. The different influences between the catalysts  $\text{TiF}_3$  and  $\text{NbF}_5$  on the hydrogen storage behavior and microstructure of the composites were investigated by XRD, SEM, TEM and hydrogen absorption/desorption tests. The as-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys contain the major phase Mg, the secondary phase  $\text{Mg}_2\text{Ni}$ , a small amount of  $\text{MgZn}_2$ ,  $\text{TiF}_3$  and  $\text{NbF}_5$ . After hydrogenation,  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  are formed, which convert back into Mg and  $\text{Mg}_2\text{Ni}$  after dehydrogenation indicating that  $\text{MgZn}_2$  and the catalysts  $\text{TiF}_3$  and  $\text{NbF}_5$  do not react with hydrogen. Compared with  $\text{NbF}_5$  catalyzed alloy, the  $\text{TiF}_3$  catalyzed alloy has a faster hydrogen absorption/desorption kinetics. On the basis of Arrhenius equation, the dehydrogenation activation energy values of the as-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys are 75.514 and 82.367  $\text{kJ mol}^{-1} \text{H}_2$ , respectively, while the value of ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  alloy is 109.830  $\text{kJ mol}^{-1} \text{H}_2$ . As a result, both  $\text{TiF}_3$  and  $\text{NbF}_5$  can significantly ameliorate the hydrogen storage thermodynamics.  $\text{TiF}_3$  shows better catalytic influence on hydrogen storage property of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  than  $\text{NbF}_5$ .

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## Introduction

For nearly half a century, rapid economic development and energy crisis have threatened our existence because of excessive exploitation of non-renewable energy sources. Meanwhile, the consequent environmental problems arising from the excessive use of fossil fuels are becoming increasingly prominent. There is a growing demand for a new kind of renewable energy. Therefore, many scholars pay attention to hydrogen owing to its high efficiency, environment friendly nature, and renewable characteristics.<sup>1–13</sup> However, the problem that is severely restricting the application of hydrogen is availability of a safe and credible storage mode.<sup>14–16</sup> Because of the merits of high gravimetric storage density and safety, many researchers have great expectations from metal hydrides as a hydrogen storage material.<sup>15–20</sup> Most researchers believe that among the different metals which can form hydrides, Mg is the most potential candidate to be widely used as a hydrogen storage material because of its low price, excellent reversibility, abundance, and high gravimetric hydrogen storage densities (7.6 wt%),<sup>21,22</sup> However at the same time, the inherent shortcomings of Mg, such as the high decomposition temperature of its hydride and poor storage kinetics seriously impede its commercial

development. Therefore, it is essential to ameliorate the kinetics and thermodynamics of the hydrogen storage alloys.

Some researches have confirmed that alloying Mg with transition metals such as Ni,<sup>23–25</sup> Zn,<sup>26,27</sup> Ti, Cr, Nb, Cu and Fe<sup>28–31</sup> can enhance the hydrogenation/dehydrogenation rates. Also, some rare earth elements,<sup>32–34</sup> intermetallic compounds,<sup>35</sup> metallic oxides,<sup>36,37</sup> and fluorides<sup>38–40</sup> are proven to have a good catalytic effect on accelerating the storage and release of hydrogen. Yavari *et al.*<sup>41</sup> added  $\text{FeF}_3$  into  $\text{MgH}_2$  to manufacture nanostructured  $\text{MgH}_2$  composites and found that hydrogenation/dehydrogenation rates were clearly enhanced. Lee *et al.*<sup>42</sup> synthesized  $\text{Mg-5NbF}_5$  and showed that  $\text{Mg-5NbF}_5$  had faster initial hydrogen absorption and desorption and a larger effective storage capacity. Ma *et al.*<sup>39</sup> mechanically prepared a  $\text{MgH}_2 + \text{TiF}_3$  system and proved that mechanical milling with 4 mol%  $\text{TiF}_3$  could enhance the sorption kinetics markedly and reduce operation temperatures in particular. The hydrogenation could be accomplished in about 25 s even at 313–373 K. Recham *et al.*<sup>43</sup> showed that  $\text{NbF}_5$  could reduce the dehydrating temperature while enhancing the kinetics of ball-milled  $\text{MgH}_2$  with 2 mol% of  $\text{NbF}_5$  as the optimum concentration. It is believed that the transition metal fluorides play a key role in enhancing the hydrogenation kinetics of Mg.<sup>42</sup>

In this study, we designed a new kind of Mg based  $\text{Mg}_{85}\text{-Zn}_5\text{Ni}_{10}$  ternary alloy, and ball milled it with  $\text{TiF}_3$  and  $\text{NbF}_5$  as catalysts to ameliorate the hydrogen storage properties. We also thoroughly investigated the influence of doping  $\text{TiF}_3$  and  $\text{NbF}_5$  on the microstructure and hydrogen storage performances of experimental materials. The storing and releasing characteristics and activation energies were also analysed.

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## Experimental

Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> alloy was prepared using a vacuum induction furnace under 0.04 MPa helium atmosphere. Extra 10 wt% Mg was added to reduce the volatilization of magnesium during melting. The as-cast alloy ingots were mechanically crushed into powders (particle size < 75 μm). Then the as-cast alloy powder was mixed with 4 wt% TiF<sub>3</sub> and NbF<sub>5</sub> and transferred to a mechanical ball mill. A planetary-type mill was used under an Ar atmosphere for milling. The weight ratio of the alloy powder and Cr–Ni stainless steel balls was 1 : 40. The milling speed was 350 rpm. During ball milling, in order to prevent excess heating, the mill was set to rest for 1 h after every 1 h of working. The samples were milled for a total of 5 h. The as-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> + 4 wt% C (C = TiF<sub>3</sub> and NbF<sub>5</sub>) in this research are named as Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>). Phase structures, morphologies and crystalline states of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> + 4 wt% C (C = TiF<sub>3</sub> and NbF<sub>5</sub>) alloys were investigated and observed by X-ray diffraction (XRD) (D/max/2400), SEM and high resolution transmission electron microscopy (HRTEM) (JEM-2100F).

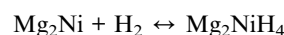
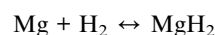
A Sieverts-type apparatus was used to measure the pressure-composition isotherms (P–C–I) and hydrogen absorption/desorption kinetics. First, 6 hydrogen absorption and desorption cycles were performed at 360 °C to completely activate the samples. PCI curves were tested at 360, 340 and 320 °C. The hydrogen absorption was conducted at a hydrogen pressure of 3 MPa, at 360, 340, 320, 300, 280, 260, 240, 220, 200 and 150 °C respectively. The hydrogen desorption was tested at a pressure of 1 × 10<sup>-4</sup> MPa at 360, 340, 320, 300 and 280 °C.

The dehydrogenation process of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> + 4 wt% C (C = TiF<sub>3</sub> and NbF<sub>5</sub>) alloys was studied by differential scanning calorimetry (DSC) on a NETZSCH, STA 449F3 instrument. The flow rate of argon was 50 mL min<sup>-1</sup>. The hydrogen saturated-samples were gradually heated from room temperature to 500 °C with an increase of 5 °C min<sup>-1</sup>.

## Results and discussion

### Phase and microstructural characteristics

X-ray diffraction (XRD) has been utilized in studying the phase compositions and structures of ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> and Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) before and after hydrogen absorption/desorption, as described in Fig. 1. We can see that after 5 h ball milling, the broadened diffraction peaks reveal that mechanical ball milling causes the reduction of grain size and amorphization. According to Fig. 1, the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> contains three phases: Mg as the major phase, the secondary phase Mg<sub>2</sub>Ni, and a small MgZn<sub>2</sub> phase. Meanwhile, after adding TiF<sub>3</sub> and NbF<sub>5</sub>, no new phase appeared in the XRD curves, indicating no reaction occurred between the catalysts TiF<sub>3</sub> and NbF<sub>5</sub> and Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> during ball milling. Mg and Mg<sub>2</sub>Ni are still the major and the secondary phase in Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys, respectively. After hydrogen absorption, it is clear that the Mg phase is converted into MgH<sub>2</sub>. Simultaneously, Mg<sub>2</sub>Ni converts to Mg<sub>2</sub>NiH<sub>4</sub>. It is worth noting that among all three samples, only MgZn<sub>2</sub> existed after hydrogen absorption, showing that it does not react with hydrogen. After hydrogen desorption, MgH<sub>2</sub> and Mg<sub>2</sub>NiH<sub>4</sub> change into Mg and Mg<sub>2</sub>Ni, respectively. MgZn<sub>2</sub> is also found in the dehydrogenated alloys. Based on the XRD patterns, there are two reversible reactions for hydrogenation and dehydrogenation of the alloys. The reaction path ways can be inferred as follows:



The Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloy samples after hydrogen absorption and desorption were detected by HRTEM and ED, as described in Fig. 2. After ball milling with the

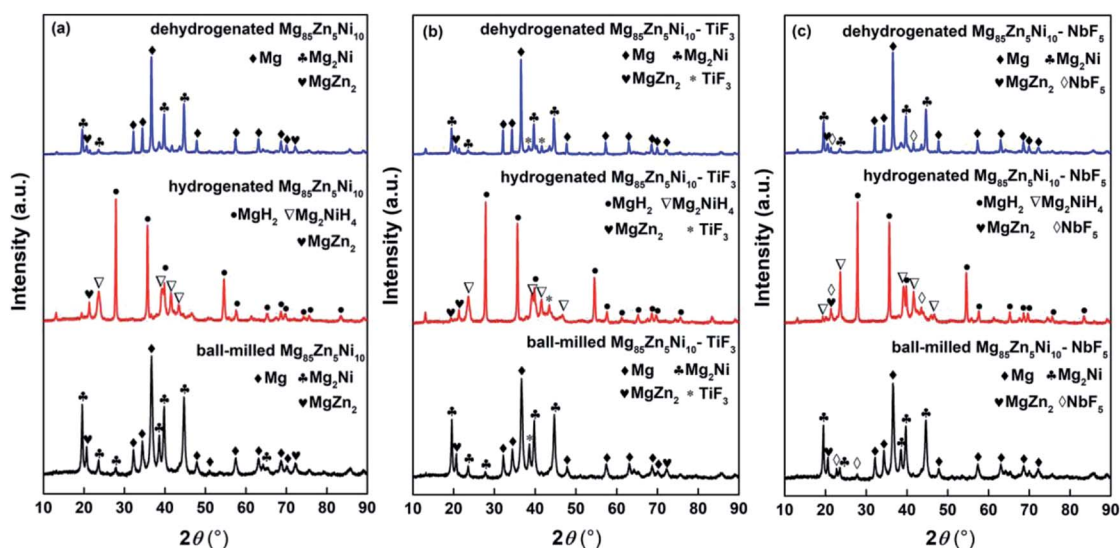


Fig. 1 XRD patterns of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub> and Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys before and after 30 hydrogen absorption and desorption cycles: (a) ball-milled, (b) C = TiF<sub>3</sub>, (c) C = NbF<sub>5</sub>.





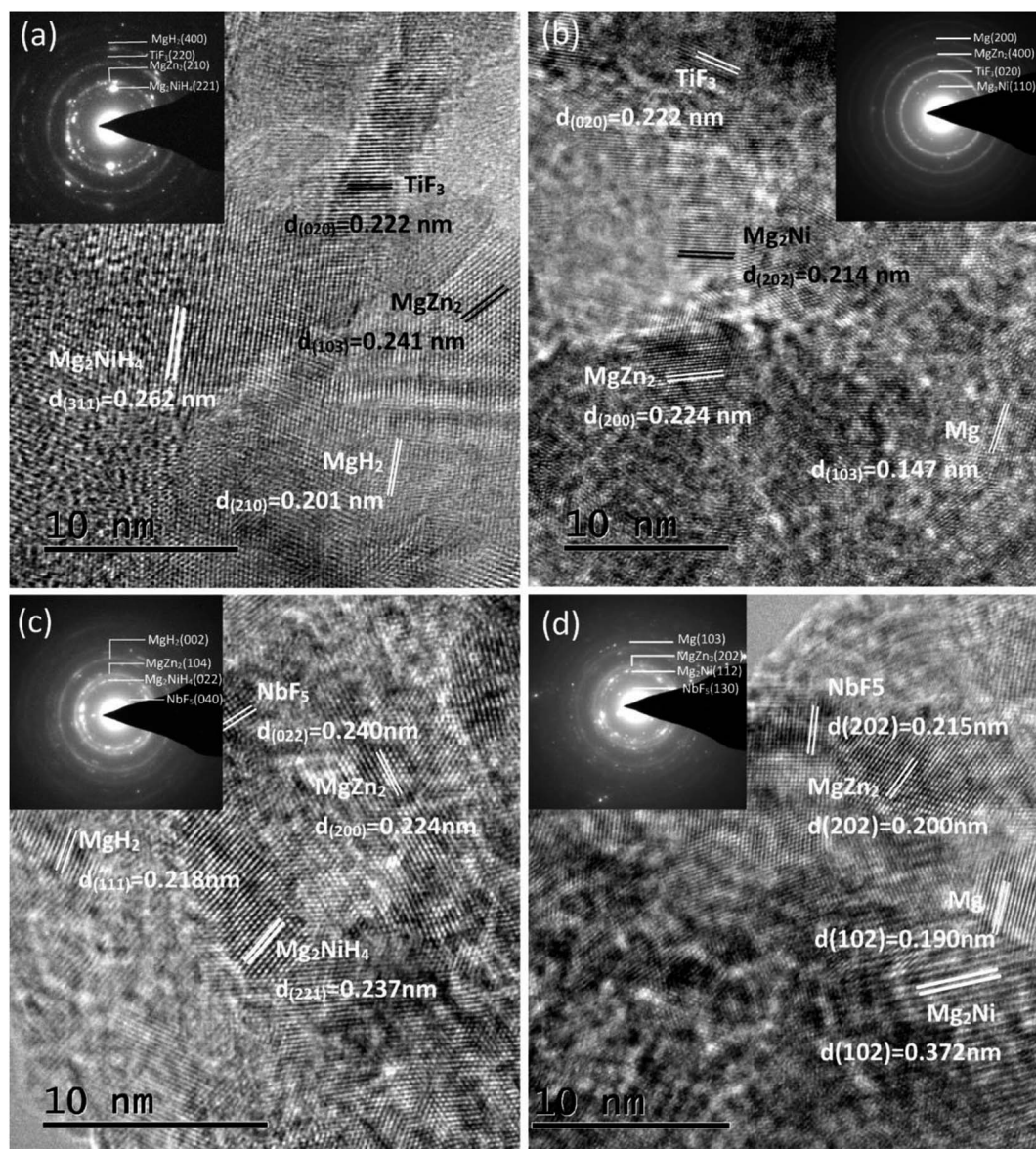


Fig. 2 HRTEM micrographs and SAED patterns of the  $Mg_{85}Zn_5Ni_{10}-4C$  ( $C = TiF_3, NbF_5$ ) alloys after hydrogen absorption and desorption: (a) hydrogenated  $C = TiF_3$ , (b) dehydrogenated  $C = TiF_3$ , (c) hydrogenated  $C = NbF_5$ , (d) dehydrogenated  $C = NbF_5$ .

catalysts and hydrogen absorption and desorption, partial nanocrystalline and amorphous phases form in the  $Mg_{85}Zn_5Ni_{10}-4C$  ( $C = TiF_3, NbF_5$ ) alloys. Evidently, after hydrogen absorption,  $Mg_{85}Zn_5Ni_{10}-4TiF_3$  contains  $MgH_2$ ,  $Mg_2NiH_4$ ,  $MgZn_2$  and  $TiF_3$  phases, and  $Mg_{85}Zn_5Ni_{10}-4NbF_5$  possesses  $MgH_2$ ,  $Mg_2NiH_4$ ,  $MgZn_2$  and  $NbF_5$  phases, which are sustained through ED patterns and also consistent with the XRD test. According to the structural analysis and index of ED rings,  $MgH_2$  and  $Mg_2NiH_4$  convert into  $Mg$  and  $Mg_2Ni$  respectively.  $MgZn_2$ ,  $TiF_3$  and  $NbF_5$  are found after hydrogen desorption, suggesting absence of reaction among  $MgZn_2$ ,  $TiF_3$ ,  $NbF_5$  and hydrogen. The catalysts  $TiF_3$  and  $NbF_5$  exist stably in the  $Mg_{85}Zn_5Ni_{10}-4C$  ( $C = TiF_3, NbF_5$ ) composites after ball milling, even after 30 hydrogenation and dehydrogenation cycles. The results of HRTEM and ED coincide with the XRD results.

Fig. 3 and 4 present the bright field FETEM images and EDS mapping of the  $Mg_{85}Zn_5Ni_{10}-4TiF_3$  and  $Mg_{85}Zn_5Ni_{10}-4NbF_5$  alloys after dehydrogenation cycles, respectively. The different colours express the distributions of different elements. As can be seen from Fig. 3(a) and (b), Mg is the major component covering the main matrix of a single  $Mg_{85}Zn_5Ni_{10}-4TiF_3$  alloy particle. In Fig. 3(c) and (d), the Ni and Zn elements are mainly distributed in the bright regions of the alloy particle illustrating that Mg–Ni and Mg–Zn metal compounds are distributed on the surface of the alloy particle. The Ti and F elements are relatively well-distributed around the alloy particle indicating uniform inlaying of  $TiF_3$  on Mg matrix which is corroborated by XRD and TEM results. Similarly, according to Fig. 4, Nb and F elements are also well-distributed on the  $Mg_{85}Zn_5Ni_{10}-4NbF_5$  alloy particles. Based on XRD, TEM and EDS mapping, the catalysts



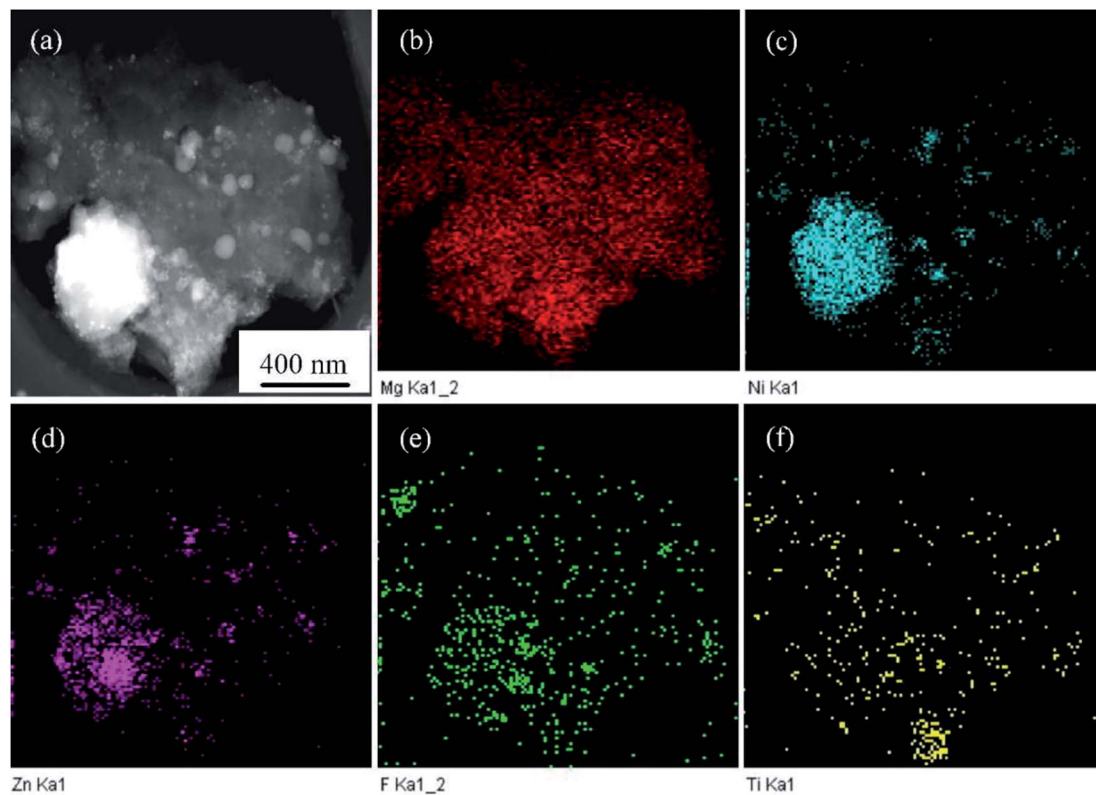


Fig. 3 FETEM micrographs and EDS mapping of the  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{TiF}_3$  alloy after hydrogen desorption cycles.

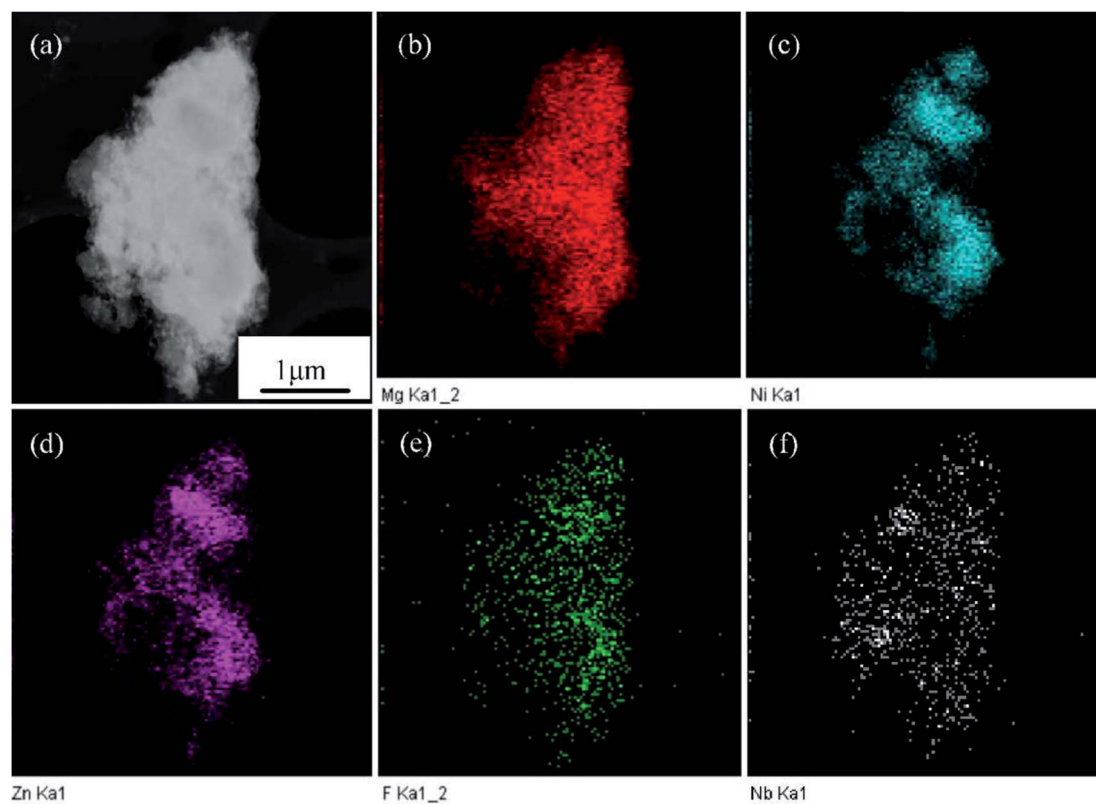


Fig. 4 FETEM micrographs and EDS mapping of the  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{NbF}_5$  alloy after hydrogen desorption cycles.





TiF<sub>3</sub> and NbF<sub>5</sub> are both present after hydrogenation and dehydrogenation cycles suggesting that they do not react with hydrogen or decompose after hydriding and dehydriding cycles.

### Hydrogenation and dehydrogenation kinetics

With the aim to study the influence of different catalysts on hydrogenation kinetics of Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>, the hydrogen absorptions of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys were measured at a pressure of 3 MPa and at 360, 340, 320, 300, 280, 260, 240, 220, 200 and 150 °C, as represented in Fig. 5. We can observe that at the beginning of the hydrogenation process, the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys have a very fast hydrogenation rate and the alloys need relatively long time to get saturated. This is because the hydride layer that is formed swiftly covers the particle surfaces and blocks the hydrogen diffusion into the alloys. For the convenience of comparison, the hydrogen absorption capacity at 600 s has been taken as the reference. According to Fig. 5, the C = TiF<sub>3</sub> alloy can absorb 4.404, 4.33, 4.238, 4.153, 4.117 wt% at 360, 340, 320, 300, 280 °C, respectively in 600 s. Simultaneously, the C = NbF<sub>5</sub> alloy can absorb 4.313, 4.244, 4.235, 4.197, 4.06 wt% at the same condition. Distinctly, the hydrogenation absorption rate within 600 s of C = TiF<sub>3</sub> alloy is a little faster than the C = NbF<sub>5</sub> alloy, also at relatively low temperatures. From Fig. 5(c) and (d), even at 150 °C, the C = TiF<sub>3</sub> alloy shows a faster absorption rate comparing with C = NbF<sub>5</sub> alloy. This explains that TiF<sub>3</sub> has

more effective catalytic effect than NbF<sub>5</sub>. The ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys show very fast hydrogenation rate. This is probably due to the TiF<sub>3</sub> and NbF<sub>5</sub> catalysts promoting H<sub>2</sub> molecules to dissociate into H atoms and distribute on the surfaces of the Mg particles. Also, after ball milling with TiF<sub>3</sub> and NbF<sub>5</sub>, the uniform mixing powders generated defects and cracks during the hydriding/dehydriding process, as illustrated in Fig. 6. These defects and cracks provide hydrogen diffusion channels and nucleation positions to form magnesium hydrides. As a comparison, the cracks formed on the C = TiF<sub>3</sub> alloy particles are evidently more than those on the C = NbF<sub>5</sub> alloy. This is the reason why the C = TiF<sub>3</sub> alloy has faster hydrogen absorption kinetics, even at relatively low temperatures.

The hydrogen desorptions of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys were tested to investigate the different catalytic effects between TiF<sub>3</sub> and NbF<sub>5</sub> on the hydrogen desorption kinetics, as depicted in Fig. 7. The hydrogen desorption from the alloys was tested at 360, 340, 320, 300 and 280 °C. Evidently, the temperature significantly affects the hydrogen desorption kinetics. The ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys have very fast desorption kinetics over 320 °C. The ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys could release all the hydrogen in less than 300 s at 360 °C, but took more than 30 minutes at 280 °C. According to Fig. 7, the time taken for releasing 4 wt% H<sub>2</sub> at 360, 340, 320, 300 and 280 °C is 102, 156, 318, 726 and 1836 s, respectively for the C =

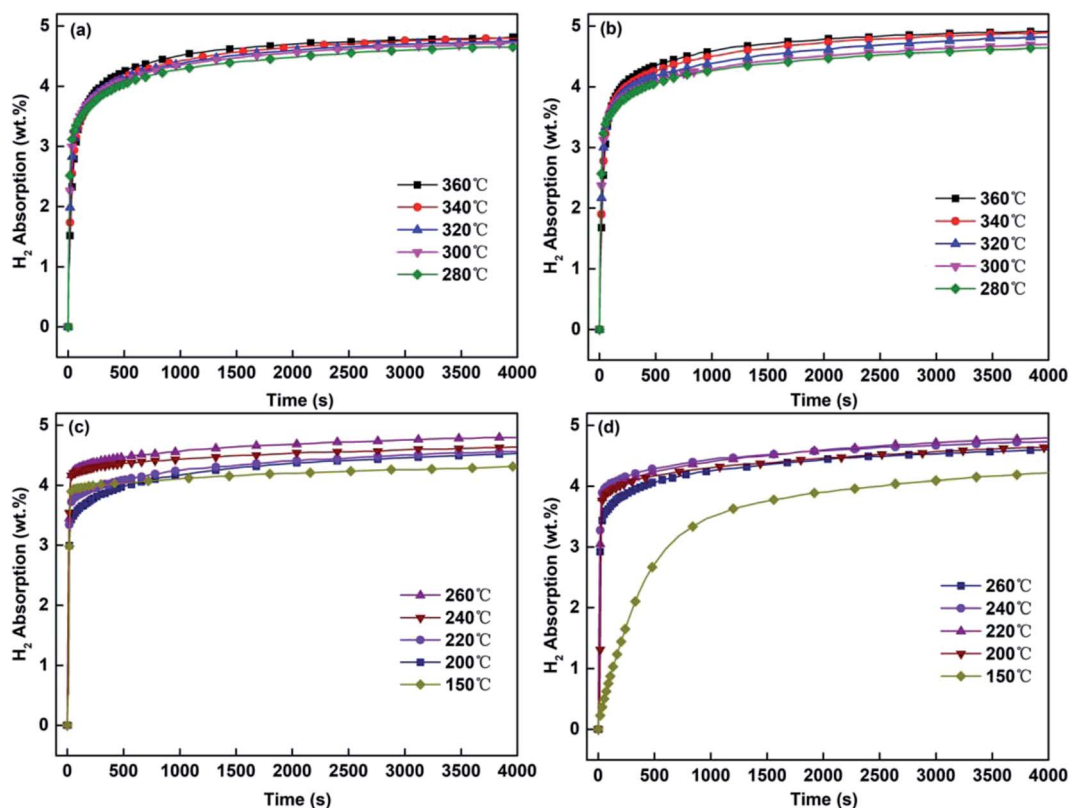


Fig. 5 Hydrogen absorption kinetic curves of the ball-milled Mg<sub>85</sub>Zn<sub>5</sub>Ni<sub>10</sub>-4C (C = TiF<sub>3</sub>, NbF<sub>5</sub>) alloys at different temperatures: (a) and (c) C = TiF<sub>3</sub>, (b) and (d) C = NbF<sub>5</sub>.



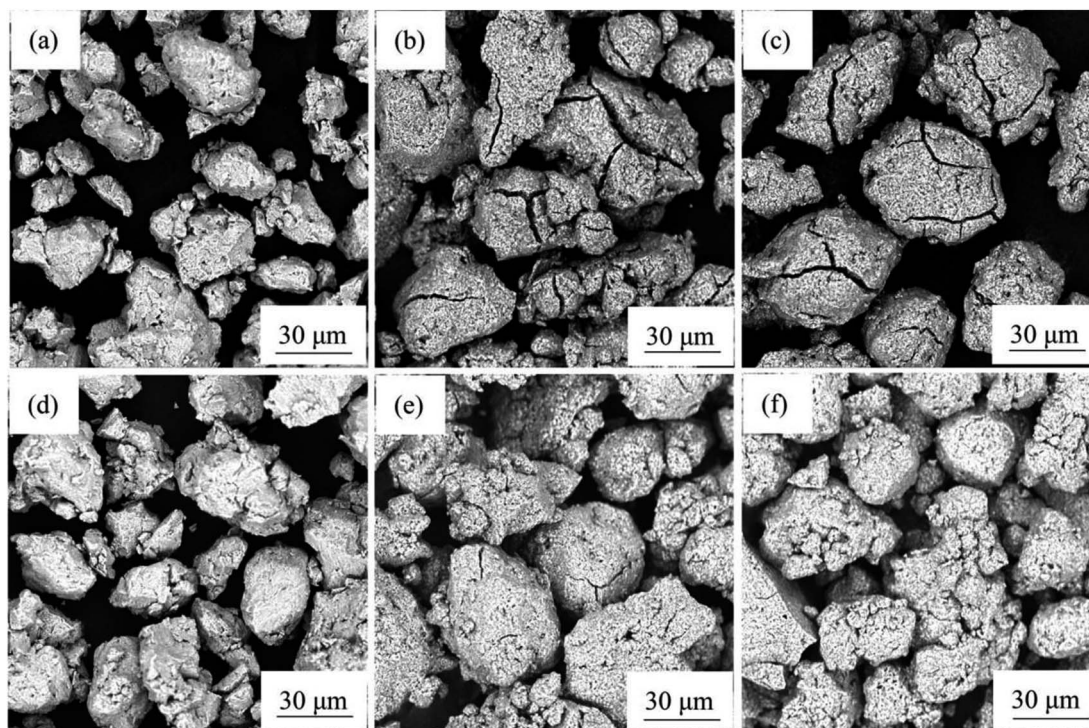


Fig. 6 SEM images of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys: (a)  $\text{C} = \text{TiF}_3$  alloy after ball milling, (b)  $\text{C} = \text{TiF}_3$  alloy after hydrogenation, (c)  $\text{C} = \text{TiF}_3$  alloy after dehydrogenation, (d)  $\text{C} = \text{NbF}_5$  alloy after ball milling, (e)  $\text{C} = \text{NbF}_5$  alloy after hydrogenation, (f)  $\text{C} = \text{NbF}_5$  alloy after dehydrogenation.

$\text{TiF}_3$  alloy, and 150, 222, 348, 756 and 1860 s, respectively for the  $\text{C} = \text{NbF}_5$  alloy. This indicates the  $\text{C} = \text{TiF}_3$  alloy has better desorption kinetics than  $\text{C} = \text{NbF}_5$  alloy owing to the defects and cracks (Fig. 6(c) and (f)) formed on the particles which promote the hydrogen diffusion. Certainly, both catalysts have significant effects on the hydrogenation kinetics compared with the milled  $\text{MgH}_2$ , which hardly decomposes at  $300^\circ\text{C}$ .<sup>44</sup>

### Hydrogen desorption property

To further study the different catalytic effects between  $\text{TiF}_3$  and  $\text{NbF}_5$  on hydrogen desorption property of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$ , the composites were characterized by DSC measurement as shown in Fig. 8. There is a big difference between the DSC curves of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys, as seen in Fig. 8. There are two endothermic peaks in the curve of  $\text{C} = \text{NbF}_5$  alloy at  $228.84^\circ\text{C}$  and  $349.93^\circ\text{C}$ . On the basis of XRD and TEM results, there are two reversible reactions in every hydrogenation and dehydrogenation reactions. The dehydrogenation reactions are  $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$  and  $\text{Mg}_2\text{NiH}_4 \rightarrow \text{Mg}_2\text{Ni} + \text{H}_2$ . Therefore, the peak at  $228.84^\circ\text{C}$  belongs to the endothermic peak of  $\text{Mg}_2\text{NiH}_4$  and the peak at  $349.93^\circ\text{C}$  corresponds to  $\text{MgH}_2$ .<sup>43,45-47</sup> However, for the  $\text{C} = \text{TiF}_3$  alloy, there seems to be only one endothermic peak at  $256.88^\circ\text{C}$  in the DSC curve. This indicates that the catalyst  $\text{TiF}_3$  strongly decreases the endothermic peak temperature of  $\text{MgH}_2$ , and even causes the two peaks of  $\text{Mg}_2\text{NiH}_4$  and  $\text{MgH}_2$  to coincide. It illustrates that the reaction for  $\text{MgH}_2$  decomposition becomes more easy by adding  $\text{TiF}_3$ . Conversely, there is no such significant catalytic effect by

$\text{NbF}_5$ . This also proves that  $\text{TiF}_3$  improves the hydrogen desorption property of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  more effectively than  $\text{NbF}_5$ . This result is in line with previous discussions of hydrogenation and dehydrogenation kinetics. Moreover, the onset temperatures of dehydrogenations are  $218.63$  and  $210.08^\circ\text{C}$  of  $\text{C} = \text{TiF}_3$  and  $\text{NbF}_5$  alloys, respectively.

### Hydrogenation and dehydrogenation cyclic stability

Fig. 9 and 10 depict the hydrogen absorbing and desorbing cyclic stability curves of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys at  $360^\circ\text{C}$ . According to Fig. 9 and 10, basically there is no change of hydrogen absorption and desorption capacities for both  $\text{C} = \text{TiF}_3$  alloy and  $\text{C} = \text{NbF}_5$  alloy after 15 cycles. It is remarkable that the hydrogenation rate of first cycle for the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys is quite slow owing to a long process of complete activation of the alloys. However, after the second cycle, the hydrogenation and dehydrogenation rates are significantly accelerated. Subsequently, with the increase of cycle times, the hydrogenation and dehydrogenation rates gradually improve and show good kinetics. This is because defects and cracks are generated during the hydrogenation and dehydrogenation cycles. These defects and cracks can provide more hydrogen diffusion channels and nucleation positions for Mg hydrides which was discussed previously. Therefore, the hydrogen absorption and desorption cyclic curves are almost identical. Also, there is no capacity loss even after 30 hydrogenation/dehydrogenation cycles. On the basis of Fig. 9 and 10, the ball-milled



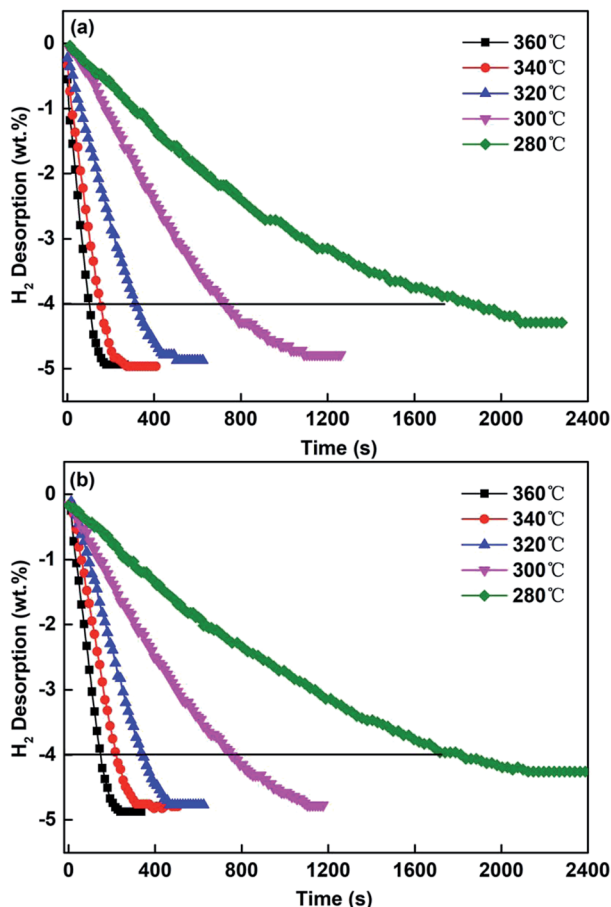


Fig. 7 Hydrogen desorption kinetic curves of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys at different temperatures: (a)  $\text{C} = \text{TiF}_3$ , (b)  $\text{C} = \text{NbF}_5$ .

$\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys reveal good hydrogenation and dehydrogenation cyclic stability. Furthermore, the capacity without any loss indicates that there is no other stable hydride formation during the hydrogenation/dehydrogenation

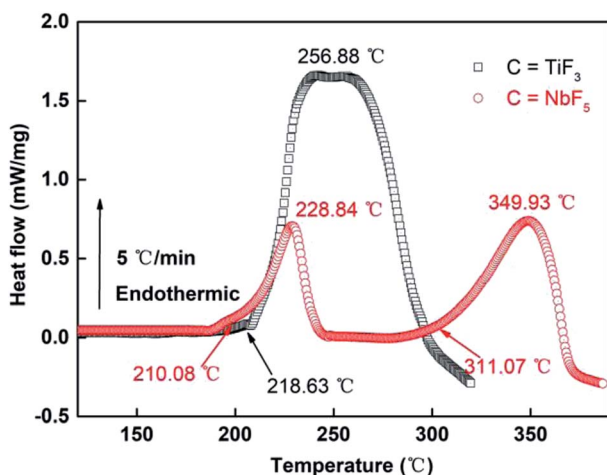


Fig. 8 DSC curves of the desorption process of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys.

process. Subsequently, the decomposition of  $\text{TiF}_3/\text{NbF}_5$  and formation of  $\text{TiH}_2/\text{NbH}_2$  is always accompanied by the loss of capacity owing to the formation of  $\text{TiH}_2$ .  $\text{TiH}_2/\text{NbH}_2$  cannot release hydrogen during dehydrogenation of  $\text{MgH}_2$ .<sup>48–50</sup> Therefore, this also proves that both  $\text{TiF}_3$  and  $\text{NbF}_5$  exist stably in the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys.

### Hydrogen desorption activation energy

In order to further study the catalytic mechanism of the differences between  $\text{TiF}_3$  and  $\text{NbF}_5$ , the dehydrogenation activation energy of the  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys is estimated by Arrhenius method. As a general rule, in a gas–solid reaction, the total energy barrier which is to be crossed determines the activation energy. The energy barrier of  $\text{H}_2$  released from  $\text{MgH}_2$  is the leading cause which may explain the dehydrogenation rate.<sup>34</sup> During hydrogenation, the activation energy is considered to be relative to the total energy barrier. As we know, the dehydrogenation reaction is accomplished by nucleation and growth processes. In addition, the Johnson–Mehl–Avrami (JMA) model always simulates the nucleation and

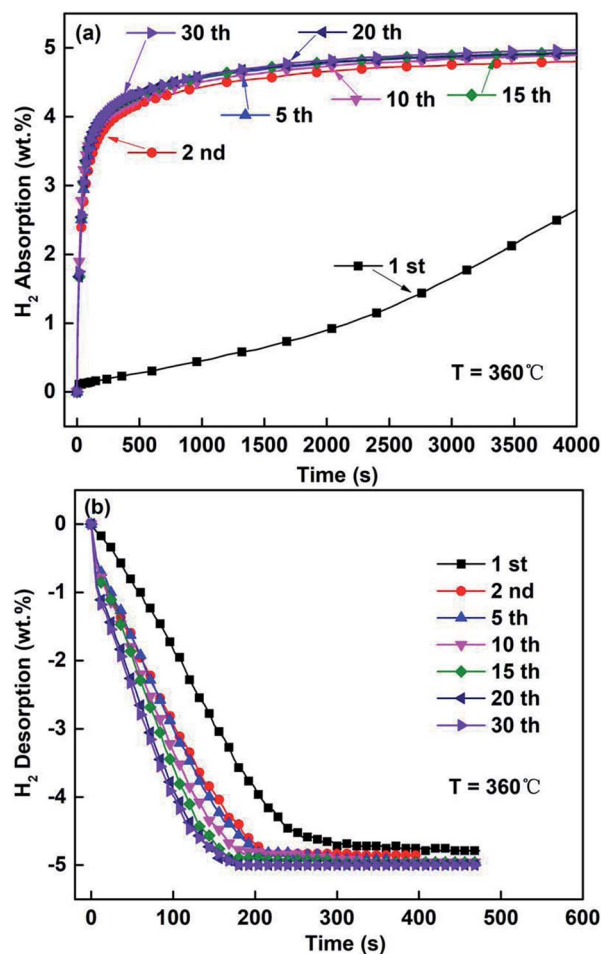


Fig. 9 Hydrogenation/dehydrogenation cycling curves of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4TiF}_3$  alloy at 360 °C: (a) hydrogenation cycles, (b) dehydrogenation cycles.





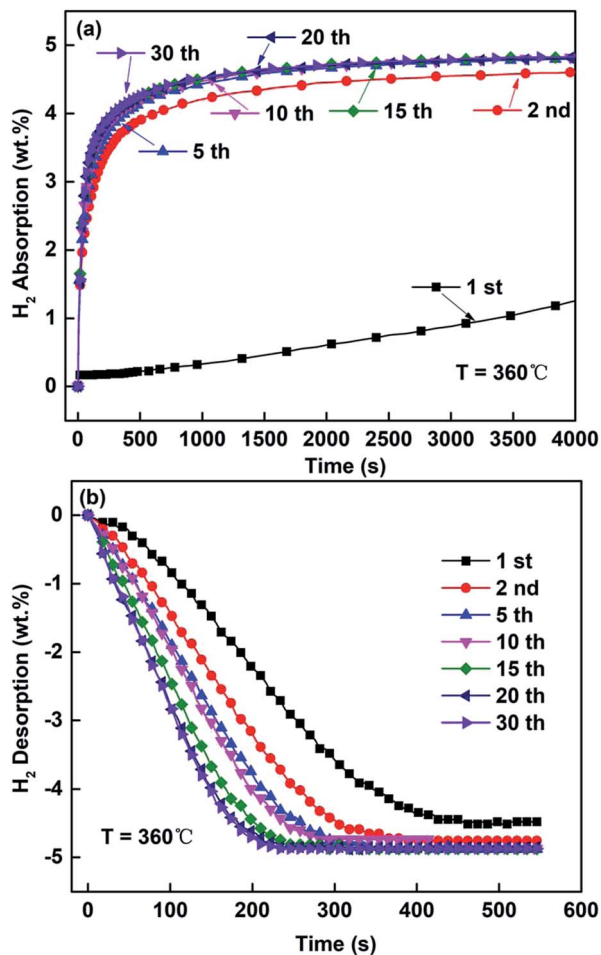


Fig. 10 Hydrogenation/dehydrogenation cycling curves of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4NbF}_5$  alloy at 360 °C: (a) hydrogenation cycles, (b) dehydrogenation cycles.

growth processes during hydrogen desorption, which is represented by the following equation:<sup>51</sup>

$$\ln[-\ln(1 - \alpha)] = \eta \ln k + \eta \ln t \quad (1)$$

where  $\alpha$ ,  $k$  and  $\eta$  represent the reaction fraction at time  $t$ , an effective kinetic parameter, and the Avrami exponent reaction order, respectively. Fig. 11 expresses the linear plots of  $\ln[-\ln(1 - \alpha)]$  vs. the  $\ln t$ . Evidently, the JMA plots described in Fig. 11 are nearly linear, illustrating that dehydriding reactions of the samples follow instantaneous nucleation followed by interface controlled-three-dimensional growth process.<sup>52</sup> According to the slope and intercept of the linear fitting,  $\eta$  and  $\eta \ln k$  values at each temperature can be calculated. On the basis of  $\eta$  and  $\eta \ln k$  values, the rate constant  $k$  is calculated, then the activation energy ( $E_a$ ) for dehydrogenation can be computed from the following Arrhenius equation:<sup>53,54</sup>

$$k = A \exp(-E_a/RT) \quad (2)$$

where,  $A$ ,  $R$  and  $T$  represent a temperature independent coefficient, universal gas constant and the absolute temperature,

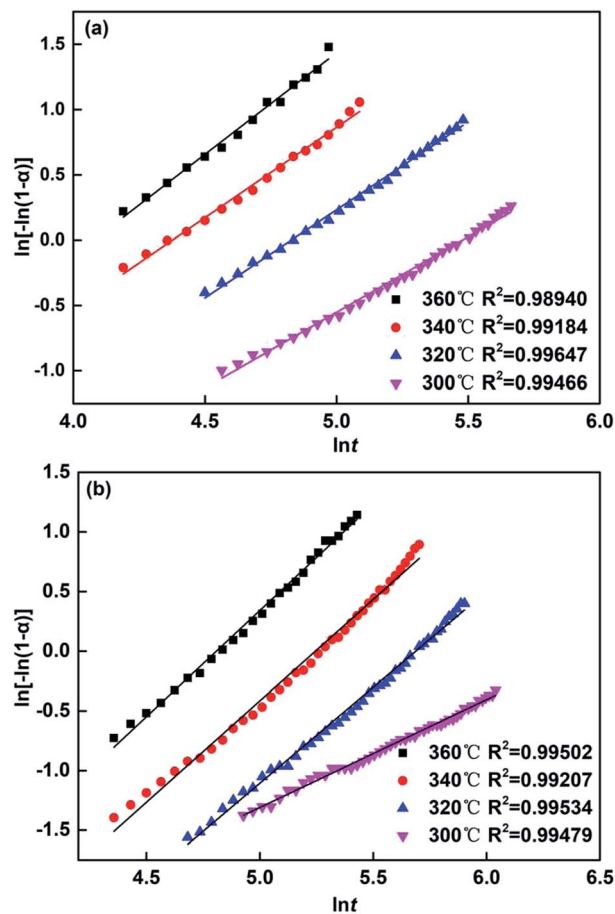


Fig. 11 JMA graphs of the as-milled and ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $C = \text{TiF}_3, \text{NbF}_5$ ) alloys at different temperatures: (a)  $C = \text{TiF}_3$ , (b)  $C = \text{NbF}_5$ .

respectively. The Arrhenius plots for the dehydrogenation kinetics are described in Fig. 12. Accordingly, on the basis of the slopes of these plots, the activation energy,  $E_a$  (de), can be calculated. The  $E_a$  (de) values of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $C = \text{TiF}_3, \text{NbF}_5$ ) alloys are 75.514 and 82.367  $\text{kJ mol}^{-1} \text{H}_2$ , respectively, and are listed in Table 1. Clearly, the  $E_a$  (de) of  $C = \text{TiF}_3$  alloy is much lower than that of the  $C = \text{NbF}_5$  alloy. In this study, the  $E_a$  (de) value of ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  is calculated to be 109.83  $\text{kJ mol}^{-1} \text{H}_2$ , suggesting that both catalysts remarkably decreased the dehydriding activation energy when compared with the  $E_a$  (de) value of pure milled  $\text{MgH}_2$  (158.5  $\text{kJ mol}^{-1} \text{H}_2$ ).<sup>55</sup>

### Hydrogen storage thermodynamics

The pressure-composition Isotherms (PCI) tests were measured at 360, 340 and 320 °C for the sake of studying the influence of different catalysts on the hydrogen storage thermodynamics of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $C = \text{TiF}_3, \text{NbF}_5$ ) alloy. The PCI curves are represented in Fig. 13. Evidently, in each PCI curves there are two distinct plateaus. The lower pressure plateau belongs to  $\text{MgH}_2$ , and the higher one is the pressure plateau of  $\text{Mg}_2\text{NiH}_4$  according to the reported results for  $\text{Mg-10Ni-xMm}$





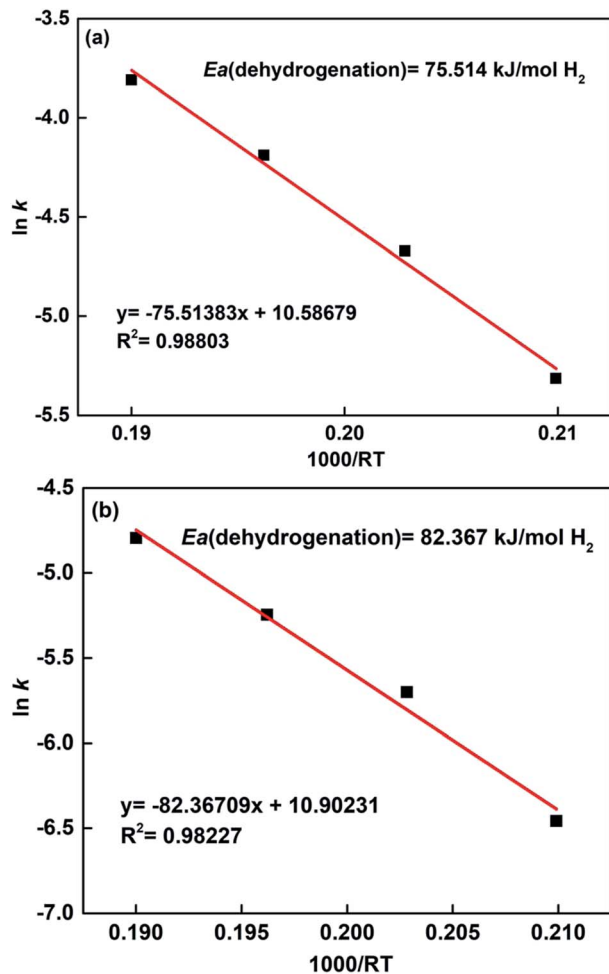


Fig. 12 P–C–I curves of the as-milled of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys at different temperatures: (a)  $\text{C} = \text{TiF}_3$ , (b)  $\text{C} = \text{NbF}_5$ .

alloy.<sup>56</sup> All the curves exhibit flat plateaus. On the basis of the plateau pressures in PCI curves, both enthalpy change  $\Delta H$  and entropy change  $\Delta S$  can be derived from the Van't Hoff equation:<sup>57</sup>

$$\ln[P(\text{H}_2)/P_0] = \Delta H/(RT) - \Delta S/R \quad (3)$$

where,  $P(\text{H}_2)$ ,  $P_0$ ,  $T$  and  $R$  represent the equilibrium hydrogen gas pressure, the standard atmospheric pressure, the sample temperature and the gas constant, respectively. Fig. 14 shows the Van't Hoff plots and the enthalpy value ( $\Delta H$ ) and entropy value ( $\Delta S$ ) of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloy. Therefore, the thermodynamic parameters can be easily

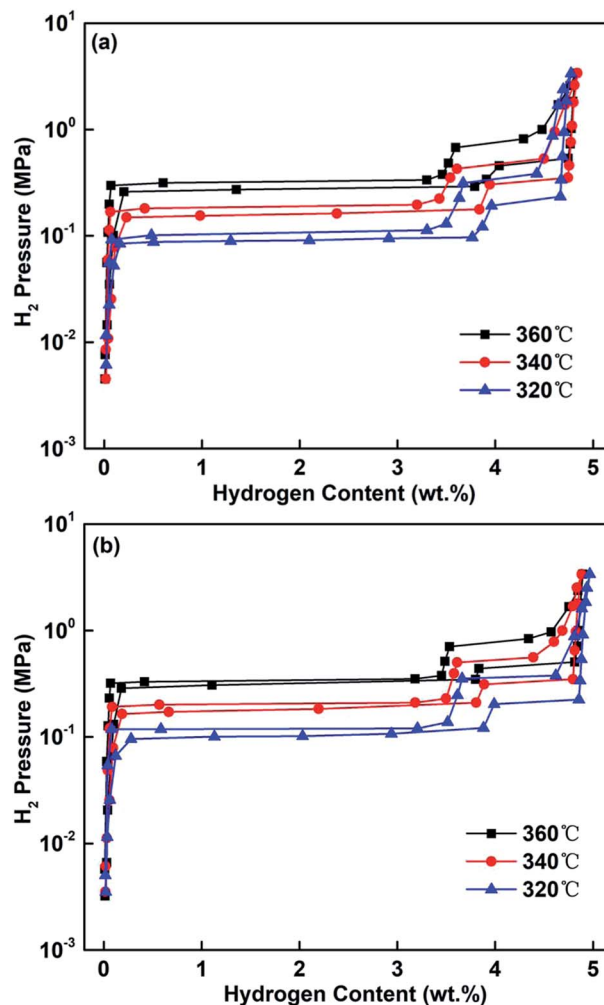


Fig. 13 P–C–I curves of the as-milled of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys at different temperatures: (a)  $\text{C} = \text{TiF}_3$ , (b)  $\text{C} = \text{NbF}_5$ .

calculated by intercepts and slopes of the Van't Hoff plots which are listed in Table 1. The calculations reveal that the hydrogen absorption/desorption  $\Delta H$  and  $\Delta S$  of the  $\text{C} = \text{TiF}_3$  alloy are smaller than of the  $\text{C} = \text{NbF}_5$  alloy indicating that  $\text{TiF}_3$  is more effective than  $\text{NbF}_5$  as a catalyst to improve the hydrogen storage thermodynamics of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$ . Meanwhile, the hydrogen absorption/desorption  $\Delta H$  and  $\Delta S$  of ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5$ ) alloys are smaller than those of ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  alloy, suggesting both  $\text{TiF}_3$  and  $\text{NbF}_5$  are helpful to ameliorate the thermodynamics of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$ .

**Table 1** Hydrogen desorption activation energy ( $E_a$  (de)), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$  ( $\text{C} = \text{TiF}_3, \text{NbF}_5, \text{none}$ ) alloy

$\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}-4\text{C}$ alloys	$E_a$ (de) ( $\text{kJ mol}^{-1}$ )	$\Delta H_{\text{ab}}$ ( $\text{kJ mol}^{-1}$ )	$\Delta S_{\text{ab}}$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$\Delta H_{\text{de}}$ ( $\text{kJ mol}^{-1}$ )	$\Delta S_{\text{de}}$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$\text{C} = \text{TiF}_3$	75.514	-70.100	-122.473	80.054	137.781
$\text{C} = \text{NbF}_5$	82.367	-75.869	-128.945	79.005	132.683
$\text{C} = \text{none}$	109.830	-82.446	-140.628	86.187	146.114



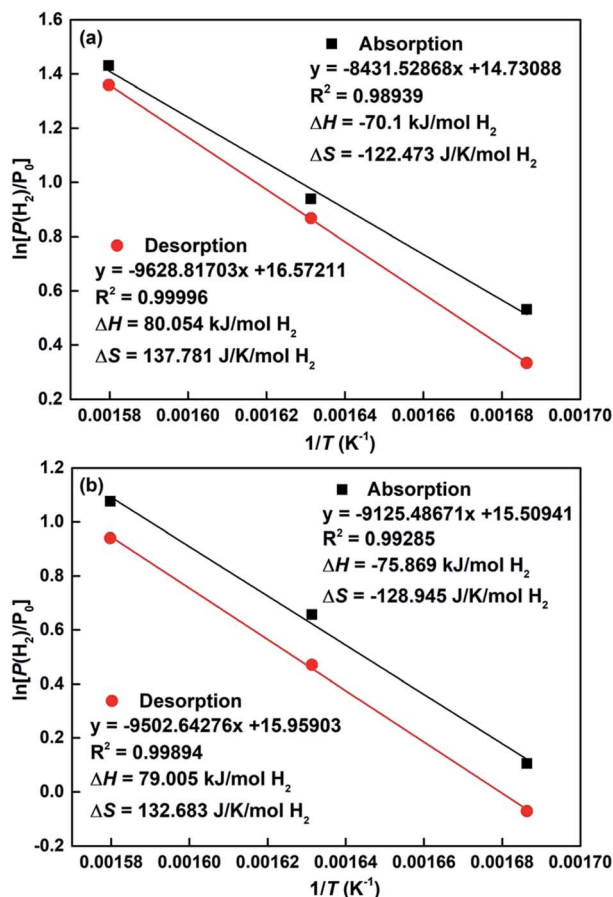


Fig. 14 Van't Hoff plots of the as-milled of the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3$ ,  $\text{NbF}_5$ ) alloys at different temperatures: (a)  $\text{C} = \text{TiF}_3$ , (b)  $\text{C} = \text{NbF}_5$ .

## Conclusions

In this investigation, as-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3$ ,  $\text{NbF}_5$ ) specimens have been prepared successfully *via* ball milling. The different influences between the catalysts  $\text{TiF}_3$  and  $\text{NbF}_5$  on the microstructure and hydrogen storage properties were studied. The main conclusions drawn are as follows:

(1) After 5 h ball milling, and 30 hydrogenation/dehydrogenation cycles, the catalysts  $\text{TiF}_3$  and  $\text{NbF}_5$  always exist in the  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3$ ,  $\text{NbF}_5$ ) composites, indicating that both  $\text{TiF}_3$  and  $\text{NbF}_5$  do not decompose and have a good stability.

(2) The  $\text{C} = \text{TiF}_3$  alloy possesses a faster hydrogen absorption/desorption rate than the  $\text{C} = \text{NbF}_5$  alloy. The dehydrogenation activation energy values calculated by Arrhenius equation of the as-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}\text{-4C}$  ( $\text{C} = \text{TiF}_3$ ,  $\text{NbF}_5$ ) alloys are 75.514 and 82.367  $\text{kJ mol}^{-1} \text{H}_2$ , respectively, while the value of ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  alloy is 109.830  $\text{kJ mol}^{-1} \text{H}_2$ , indicating that the catalysts  $\text{TiF}_3$  and  $\text{NbF}_5$  visibly reduce the dehydrogenation activation energy and effectively improve the hydrogen absorption/desorption kinetics.

(3) Compared with the ball-milled  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  alloy, the composites catalyzed by  $\text{TiF}_3$  and  $\text{NbF}_5$  possess lower

thermodynamic parameters ( $\Delta H$  and  $\Delta S$ ), suggesting that  $\text{TiF}_3$  and  $\text{NbF}_5$  can significantly ameliorate the hydrogen storage thermodynamics.

(4)  $\text{TiF}_3$  has a better effect to generate more defects and cracks during the hydriding/dehydriding process than  $\text{NbF}_5$ , which is responsible for the faster hydrogen absorption/desorption rate. During hydrogenation and dehydrogenation, defects and cracks existing on alloy particles play an effective and important role in increasing the hydrogen absorption and desorption rates.  $\text{TiF}_3$  has a better catalytic effect on the hydrogen storage property of  $\text{Mg}_{85}\text{Zn}_5\text{Ni}_{10}$  than  $\text{NbF}_5$ .

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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