Catalytic effect of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) on hydrogen storage properties of ultrafine magnesium particles†

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In order to improve hydrogen storage properties of magnesium, \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) (TiMn2 type) alloy particles have been added into magnesium ultrafine particles produced by a hydrogen plasma-metal reaction approach by ball milling. The \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) particles are uniformly dispersed on the surface of magnesium. The addition of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy improves both the hydrogen storage capacity and kinetics of magnesium. The magnesium–5 wt\% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite can absorb 6.00 wt\% H\(_2\) within 60 minutes at 523 K and desorb 6.00 wt\% H\(_2\) within 15 minutes at 623 K. With the increase of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) the hydrogenation and dehydrogenation kinetics of the composites improve. The apparent activation energies of magnesium–x wt\% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) (x = 5, 10, 30) composites for hydrogen absorption and desorption are 67.52, 65.80, 60.99 kJ mol\(^{-1}\) and 121.37, 116.68, 77.25 kJ mol\(^{-1}\), respectively. The enhanced hydrogen storage capacities and kinetics can be attributed to the effective catalysis of the \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy and ultrafine size of magnesium particles.

**Introduction**

With fossil fuel resources rapidly depleting, searching for alternative energy resources is becoming an increasingly common concern for governments and scientists worldwide. Hydrogen, as a kind of pollution-free, high-energy-density and recyclable secondary energy carrier, is one of the most promising candidates to substitute fossil fuels in the future. Conventional storage of compressed hydrogen under high pressure is of low gravimetric and volumetric H\(_2\) density, making it difficult to reach the targets of the DOE. Of the various hydrogen storage methods, storing hydrogen using solid-state materials has the advantages of suitable storage capacity, high safety and less energy loss. Among various solid-state hydrogen storage materials, magnesium (Mg) is considered to be an attractive one for its high theoretical reversible hydrogen storage capacity (7.6 wt\%), light weight and low cost. However, the sluggish hydrogenation/dehydrogenation kinetics and the high decomposition temperature still limit its practical application for hydrogen storage.

Transition metals,7,8 oxides9−11 and hydrogen storage alloys12,13 were used as the catalysts to improve the hydrogen storage performance of Mg through ball milling technique. Among these additives, hydrogen storage alloys which can absorb and desorb hydrogen at room temperature are quite potential one for their effective catalysts on kinetics and hydrogen capacities. Generally, Mg could absorb hydrogen only at temperatures higher than 573 K with a slow hydrogenation rate. It has been reported that Mg at microscale absorbed 1.5 wt\% H\(_2\) within 2 h at 673 K.14,15 The milled Mg−TiMn\(_{1.5}\) composite absorbed hydrogen of 4.0 wt\% at 573 K in 5 min.14 A milled Mg−Ti\(_{0.28}\)Cr\(_{0.30}\)V\(_{0.32}\) composite could absorb 4.0 wt\% H\(_2\) at 548 K within 10 min.19 After ball milling for 5 hours, the Mg−V\(_{0.85}\)Ti\(_{0.05}\)Fe\(_{0.05}\) composite presented a rapid hydrogen sorption rate, which was able to uptake 4.97 wt\% H\(_2\) at 573 K within 60 min and release 5.5 wt\% hydrogen at 623 K within 40 min.20

Among the hydrogen storage alloys, the TiMn\(_2\) type alloys21 with excellent hydrogen storage properties at room temperature are seldom studied as an additive for Mg-based hydrogen storage material, let alone the consideration of their content on the performance of Mg.

Although high energy ball milling can reduce the grains of Mg particles to nanosize, their particle sizes are still in the range of micrometers.22,23 It has been demonstrated that the sorption kinetics of Mg can be significantly enhanced when its size is reduced to nanoscale.24−29 Thus, using Mg ultrafine particles (UFPs) and doping TiMn\(_2\) type alloys are expected to improve...
the comprehensive hydrogen storage performance of Mg. Hydrogen plasma-metal reaction (HPMR) approach is often used to produce metallic UFPs at large scale and with high purity. Recently, Mg and Mg-based composite UFPs, such as Mg–Al, Mg–Ti–V, and Mg–Nb, have been successfully prepared through HPMR technique.30–32 Recently, we prepared a kind of TiMn2 type alloy ((Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1) with good hydrogen storage properties at room temperature. In this work, we intend to fabricate the Mg–x wt% TiMn2 (x = 0, 5, 10, 30) composites by milling the Mg UFPs produced by HPMR with the TiMn2 alloy, investigate their hydrogen storage properties and the effects of content of TiMn2 alloy on the performance of Mg, and clarify the catalytic mechanism of the TiMn2 alloy for improving the hydrogenation and dehydrogenation properties of Mg in detail.

Experimental
Preparation of Mg–x wt% (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 composites

The (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 alloy was prepared by arc melting of the constituent metals with the purity more than 99.5% on a water-cooled copper crucible under a high purity argon atmosphere (99.999%). An excess amount of Mn of 5 wt% was added considering the weight loss of Mn during melting due to its low melting point. The button was turned over and remelted four times to ensure high homogeneity. Then, it was mechanically crushed into several pieces and ground into powders with the stainless mortar in the glove box. The Mg UFPs were produced by HPMR method in a water-cooled chamber connected with a collecting room. The arc discharge of Mg (purity >99.5%) ingot of 20 g was performed in a mixture of hydrogen and argon in a ratio of 1 : 1 with a total pressure of 0.1 MPa. During the process, the discharge current was kept at 100 A. The UFPs were collected in Ar atmosphere. The (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 powders and Mg UFPs were mixed homogeneously with a composition of Mg–x wt% (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 (x = 0, 5, 10, 30). The mixtures were put into a stainless steel vial in the glove box and were milled under an initial pressure of 4 MPa H2 with planetary ball miller at a rotation speed of 200 rpm for 2 h and a ball-to-powder ratio of 20 : 1. The collecting and filling of the sample were operated in the glove box filled with Ar to prevent oxidation.

Characterization

The hydrogen absorption and desorption properties of the (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 and Mg–x wt% (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 (x = 0, 5, 10, 30) composites were evaluated using a Sieverts-type apparatus. Prior to the measurements, the samples of (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 alloy experienced one hydrogen absorption/desorption cycle at room temperature at the hydrogen pressure of 4 MPa and vacuum. The Mg–x wt% (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 (x = 0, 5, 10, 30) composites were activated by one hydrogen absorption/desorption cycle at 400 °C at the hydrogen pressure of 4 MPa and vacuum. The initial hydrogen pressures for hydrogenation/dehydrogenation were selected as 4 MPa and 100 Pa at each temperature. The pressure–composition–temperature (PCT) curves at different temperatures (623, 648, and 673 K) were plotted using the conventional pressure–volume–temperature technique to investigate the thermodynamic property of the composites. The hydrogen absorption or desorption measurement for the PCT curves was considered as reaching equilibrium when the vibration of hydrogen pressure at the certain temperature was less than 20 Pa s–1. The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku X-ray diffractometer with monochromatic Cu Kα radiation. Scanning electronic microscope (SEM) was applied to analyze the morphology of the samples. An energy dispersive spectroscopy (EDS) detector was used to determine the elemental distributions.

Results and discussion
Sample characterization

Fig. 1a displays the typical hexagonal shape of Mg UFPs fabricated by the HPMR method with an average particle size of 300 nm. It can be observed from Fig. 1b that the as-prepared Mg UFPs have single α-Mg phase (JCPDS no. 35-0821, space group P63/mmc). The as-prepared ((Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 particles consist of single C14-Laves phase (JCPDS no. 50-1114, space group P63/mmc), see Fig. 1c.

Fig. 1 TEM image of the Mg UFPs fabricated by the HPMR method (a) and XRD patterns of the as-prepared Mg UFPs (b) and (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 particles (c).
After ball milling process, the Mg–TiMn2 alloy composites with different percentage of \((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) show similar morphologies. Fig. 2a displays the SEM image of the as-milled Mg–30 wt% \((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) composite as an example. It can be seen that the particle size varies from 100 to 500 nm with an average of about 200 nm. The as-milled Mg–\((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) particles were nearly spherical in shape, which was different from the pure Mg UFPs prepared by HPMR with a clear hexagonal shape (see Fig. 1a). Since \((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) is brittle, we suppose that the TiMn2 type alloy powders are broken and cover on the Mg UFPs after ball milling. It is interesting to find that the particle size and morphology of the composite sample stay unchangeable after hydrogenation and dehydrogenation cycles, see Fig. 2b.

Fig. 2  SEM images of the Mg–30 wt% \((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) composite: (a) as-milled and (b) after hydrogenation and dehydrogenation cycles.

Fig. 3  High magnification SEM image of the Mg–30 wt% \((Ti_{0.85}Zr_{0.15})_{1.05}Mn_{1.2}Cr_{0.6}V_{0.1}Cu_{0.1}\) composite (a) and EDS maps of Mg (b), Mn (c), Ti (d), Cr (e), Zr (f), V (g), Cu (h).
To further reveal the morphology and elements distribution of Mg–(Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 composite, high magnification SEM and EDS analyses were conducted. Fig. 3a displays the SEM image of Mg–30 wt% (Ti0.85Zr0.15)1.05–Mn1.2Cr0.6V0.1Cu0.1 composite after ball milling. A large number of small particles can be seen clearly on the coarse surface of large particles. EDS mapping results (Fig. 3b–h) show that the composite particle is dominantly made of Mg together with (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1Cu0.1 composite and the samples K. Three strong di–obtained a–homogeneously on the surface of Mg particles. The Mg–in this work, 4 weak di–displays the SEM image of Mg–magni–high cooling rate.

The Mg–suppressed by the low hydrogen pressure (0.05 MPa) and the formation of magnesium hydride during the HPMR process is sorption kinetics and thermodynamics. It was reported that the hydride of Mg can be formed is determined by its hydrogen fraction peaks of MgH2 (JCPDS no. 12–33) can be found in Fig. 4a, which agree well with the as-prepared Mg UFPs sample in Fig. 1b. Four weak diffraction peaks at 39.58°, 43.05°, 43.89° and 44.85° can also be found in Fig. 4a, which are in good accordance with the peaks of the as-prepared Mg UFPs sample in Fig. 1c. It is known that whether the hydride of Mg can be formed is determined by its hydrogen sorption kinetics and thermodynamics. It was reported that the formation of magnesium hydride during the HPMR process is suppressed by the low hydrogen pressure (0.05 MPa) and the high cooling rate. In this work, no hydride can be found in the XRDMg–5 wt% (Ti0.85Zr0.15)1.05–Mn1.2Cr0.6V0.1Cu0.1 composite transforms completely into MgH2 after hydrogenation at 673 K. After the dehydrogenation at 673 K, MgH2 completely transforms into Mg (see Fig. 4c). The Mg–appears to be stable during the hydrogenation and dehydrogenation process (see Fig. 4b and c), suggesting that (Ti0.85–Zr0.15)1.05–Mn1.2Cr0.6V0.1Cu0.1 does not react with Mg, nor does it react with MgH2. Therefore, the (Ti0.85Zr0.15)1.05–Mn1.2Cr0.6V0.1Cu0.1 dopant plays a role of catalyst during both the hydrogenation and dehydrogenation processes of Mg. Zhou et al. also found Ti0.9Zr0.2Cr0.6V0.1Cu0.1 phase in Mg–TiMn2 composite stayed stable during the hydrogen absorption and desorption process acting as a catalyst. Fig. 5a shows that the prepared Mg–10 wt% (Ti0.85–Zr0.15)1.05–Mn1.2Cr0.6V0.1Cu0.1 composite also consists of Mg,
MgH₂ and C14 Laves phases. As shown in Fig. 5b and c, Mg fully transforms into MgH₂ after hydrogenation at 673 K, and MgH₂ releases H₂ completely and transforms into Mg after dehydrogenation at 673 K. The C14-(Ti₀·₈₅Zr₀·₁₅)₁·₀₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite phase also keeps stable during the hydrogenation and dehydrogenation process (see Fig. 5b and c). Compared Fig. 4a–c for Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅)₁·₀₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite, the peak intensities of (Ti₀·₈₅Zr₀·₁₅)₁·₀₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁-C14 Laves phase in Fig. 5a–c are stronger due to the increasing content.

Fig. 6a represents that the prepared Mg–30 wt% (Ti₀·₈₅–Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite contains the same phases as the samples with 5 wt% and 10 wt% TiMn₂ alloy. Mg transforms into MgH₂ (as shown in Fig. 6b) after absorbing hydrogen at 673 K and then transforms completely into Mg after desorbing hydrogen at 673 K (see Fig. 6c). The (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ alloy keeps its phase unchanged during the testing process. It can be seen from Fig. 6d that the intensities of the diffraction peaks of (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁-C14 Laves phase are much stronger comparing with the composites with 5 wt% and 10 wt% TiMn₂ alloy, and more weak peaks such as 48.05°, 73.71° and 77.76° can be seen clear in Fig. 6b and c.

Hydrogen storage properties

To further understand the catalytic effect of (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ on the hydrogen properties of Mg, the hydrogen absorption and desorption capacities and kinetics are measured by a carefully calibrated Sieverts-type apparatus. Hydrogen content (wt%) is the weight ratio of hydrogen and the Mg-(Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composites. The hydrogenation curves at various temperatures with an initial hydrogen pressure of 4 MPa are presented in Fig. 7. It can be observed from Fig. 7a that the ball milled Mg UFPs can quickly uptake 6.00 wt% hydrogen within 5 min at 673 K and uptake 5.50 wt% hydrogen within 2.5 min at 623 K. However, without milling, the Mg UFPs need 10 min at 673 K and 20 min at 623 K to absorb the same amount hydrogen. The ball milled Mg UFPs have hydrogenation capacities of 5.93 wt% at 573 K and 5.83 wt% at 523 K, much higher than that of the Mg UFPs without milling, whose hydrogenation capacities are only 4.82 wt% at 573 K and 4.41 wt% at 523 K. Generally, fresh surface areas can be generated in Mg during the milling process. The higher hydrogenation capacity and better kinetics for the ball milled Mg UFPs are attributed to the fresh surface areas, whose oxide layers may be removed during the milling process.

It is observed in Fig. 7b that Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite has a high hydrogen absorption capacity of 6.54 wt% and can quickly absorb 6.00 wt% H₂ within 100 s at 673 K, showing better kinetics and capacity than the ball milled pure Mg UFPs, which has a hydrogen absorption capacity of 6.25 wt% and needs 300 s to uptake 6.00 wt% hydrogen at 673 K. This indicates that the (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ alloy catalyzes the hydrogenation process of Mg. The reduced particle size of Mg in the Mg–TiMn₂ composite compared with Mg UFPs without milling should increase the surface area, which may also attribute to the improved hydrogen storage performance to some extent. On the other hand, the particle sizes of the ball milled Mg with and without TiMn₂ alloy are comparable, we suggest that the improved performance of the Mg–x wt% TiMn₂ (x = 5, 10, 30) samples in comparison with the pure Mg sample after ball milling are mainly attributed to the catalytic effect of TiMn₂ alloy. In addition, it takes more than 120 s for Mg–Nb nanocomposite prepared by HPMR to reach a value of 6.00 wt% H₂ under the same condition. It is also observed that the Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite is able to absorb 6.00 wt% H₂ within 5 min at 623 K, superior to Mg–7 at% Al nanoparticles synthesized by the HPMR method that only absorbed 5.41 wt% H₂ within 5 min at 623 K. These results demonstrate the superior catalytic effects of (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ alloy. The Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite can also rapidly absorb 5.50 wt% H₂ in 5 min and reach a final value of 6.10 wt% at 573 K, higher than the Mg–5 at% Ti₀·₉₈Zr₀·₀₂V₀·₄₃Fe₀·₀₉Cr₀·₀₉Mn₁·₅ composite prepared by milling commercial MgH₂ (tens micrometer-scale particle size) with Ti₀·₉₈Zr₀·₀₂V₀·₄₃Fe₀·₀₉Cr₀·₀₉Mn₁·₅ alloy, which absorbed a total of 5.5 wt% H₂ at 573 K. This suggests that the enhanced hydrogenation properties of the Mg–(Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composites are also relate to the ultrafine size of Mg which shortens the diffusion distances in the sorption process. The storage capacity of the Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite reaches 6.00 wt% H₂ within 60 min at 523 K, higher than the Mg–Ti–V nanoparticles which absorbs 5.00 wt% in 60 min at 523 K. The hydrogen absorption capacity of the Mg–5 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite decreases dramatically from 3.78 wt% to 0.68 wt% with the temperature dropping from 473 K to 423 K, which is still much higher than that of the ball milled pure Mg UFPs which only absorb 1.47 wt% and 0.06 wt% H₂ at 473 K and 423 K respectively (see Fig. 7a).

It can be seen from Fig. 7c that the Mg–10 wt% (Ti₀·₈₅Zr₀·₁₅),₅Mn₁·₂Cr₀·₆V₀·₁Cu₀·₁ composite has hydrogenation capacities of 5.72, 5.52, 5.14, 4.69 and 2.90 wt% H₂ at 673, 623,
573, 523 and 473 K, respectively, lower than that of the Mg–5 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite. That is due to \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy does not absorb or desorb hydrogen at the temperature above 423 K (as shown in Fig. S3†). The reaction percentage (%) for certain reaction time is calculated through dividing the hydrogen content for the reaction time by the saturation hydrogen content at different temperatures. The hydrogenation reaction percentage of Mg–10 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite within 10 min is calculated from Fig. 7c to be 84% and 41% at 523 K and 473 K respectively. However, the hydrogenation reaction percentage of the Mg–5 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite within 10 min calculated from Fig. 7b is only 75% and 32% at 523 K and 473 K respectively, indicating that the increase of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) content contributes to the improvement of hydrogenation kinetics.

Fig. 7 shows that the Mg–30 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite can absorb 4.63, 4.25, 4.19, 3.50 and 2.41 wt% \(\text{H}_2\) at 673, 623, 573, 523 and 473 K respectively, lower than the composite with 10 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy. It can be calculated from Fig. 7 that the hydrogenation reaction percentage of the Mg–30 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite at 10 min is 91% and 47% at 523 K and 473 K respectively, better than the composite with 10 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy. This implies that \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) improves the hydrogenation kinetics of Mg, and adding more \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) leads to higher hydrogenation rate but deteriorates hydrogenation capacity.

It can be concluded that adding a certain amount of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy can improve both the hydrogen absorption capacity and rate of Mg. The hydrogen absorption capacity of the Mg–\((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite decreases but its kinetics improves with the increase of \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) content.

The dehydrogenation curves of Mg–x wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) \((x = 0, 5, 10, 30)\) composites at various temperatures with an initial hydrogen pressure of 100 Pa are presented in Fig. 8. It is observed that the ball milled Mg UFPs can release 5.00 wt% \(\text{H}_2\) in 2 min at 673 K and reach a value of 6.20 wt% \(\text{H}_2\) in 60 min, much better than the Mg UFPs without milling, which can only desorb less than 5.00 wt% \(\text{H}_2\) within 60 min at the same temperature.31 It is also observed that the ball milled Mg UFPs can quickly desorb 6.00 wt% \(\text{H}_2\) in 20 min and reach a value of 6.10 wt% \(\text{H}_2\) in 60 min at 623 K, superior to the Mg UFPs synthesized by the HPMR method that released less than 4.00 wt% \(\text{H}_2\) at 623 K in 60 min.31 Obviously, the milling process significantly improves the dehydrogenation capacities and kinetics of Mg.

As shown in Fig. 8b, Mg–5 wt% \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) composite is able to quickly desorb 6.00 wt% \(\text{H}_2\) within 90 s at 673 K and within 15 min at 623 K, while it takes 250 s and 20 min for the ball milled Mg UFPs to reach the same value at 673 K and 623 K respectively, indicating that the \((\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{Cu}_{0.1}\) alloy improves the hydrogen
desorption capacities and kinetics apparently as a catalyst. In comparison with the Mg–Nb nanocomposite which needed 220 s to desorb 6.00 wt% H₂ at 673 K and 27 min to desorb 6.00 wt% H₂ at 673 K, the (Ti₀.₈₅Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₅Cu₀.₁ alloy shows superior catalytic effects on the dehydrogenation of MgH₂. The hydrogen desorption capacity of Mg–5 wt% (Ti₀.₈₅Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₅Cu₀.₁ composite within 60 min reaches 6.51 wt% H₂ at 673 K, 6.30 wt% H₂ at 623 K and 1.93 wt% H₂ at 573 K, much higher than that of Mg–Ti–V nanocomposite which desorbed 5.01 wt%, 4.02 wt% and 1.13 wt% H₂ at 673 K, 623 K and 573 K respectively. It can be deduced that the (Ti₀.₈₅Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₅Cu₀.₁ particles on the surface of MgH₂ particles effectively improve the hydrogen desorption rate and capacity of MgH₂. It can be seen from Fig. 8c that the Mg–10 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₃Cr₀.₆V₀.₁Cu₀.₁ composite has dehydrogenation capacities of 5.59 wt% H₂ at 673 K and 5.50 wt% H₂ at 623 K, lower than that of the Mg–5 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₃Cr₀.₆V₀.₁Cu₀.₁ composite due to the dead weight of (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₃Cr₀.₆V₀.₁Cu₀.₁ alloy. The Mg–10 wt% (Ti₀.₈₅Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₅Cu₀.₁ composite can desorb 2.99 wt% H₂ within 200 s at 623 K, whose dehydrogenation reaction percentage at 200 s calculated from Fig. 8c is 54.4%. In comparison, the Mg–5 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₃Cr₀.₆V₀.₁Cu₀.₁ composite can desorb 1.17 wt% H₂ within 200 s at 623 K, whose dehydrogenation reaction percentage at 200 s calculated from Fig. 8b is only 18.1%, indicating the increase of (Ti₀.₈₅Zr₀.₁₅)₁.₀₅Mn₁.₃Cr₀.₆V₀.₁Cu₀.₁ content contributes to the improvement of its dehydrogenation kinetics. Surprisingly, the Mg–10 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₅Cu₀.₁ composite can release 4.62 wt% H₂ at 673 K and 4.18 wt% H₂ at 623 K, lower than the Mg–10 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ composite with less TiMn₂ alloy. However, the Mg–30 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ composite still shows better dehydrogenation kinetics than Mg–10 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ composite. It can desorb 3.35 wt% H₂ within 200 s at 623 K, whose reaction percentage at 200 s calculated from Fig. 8d is 80.2% (54.4% for Mg–10 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ composite). At 573 K and 523 K, the Mg–30 wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ composite can release 4.42 wt% H₂ at 673 K and 3.92 wt% H₂ at 623 K.

Fig. 8 Dehydrogenation kinetics of Mg–x wt% (Ti₀.₈₂Zr₀.₁₅)₁.₀₅Mn₁.₂Cr₀.₆V₀.₁Cu₀.₁ (x = 0, 5, 10, 30) composites at 100 Pa and different temperatures.
composite can release 3.52 wt% and 0.73 wt% H$_2$ within 60 min respectively, higher than Mg–10 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite which can only desorb 2.99 wt% and 0.40 wt% H$_2$ under the same temperatures. This further supports the fact that (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloy plays an important role in promoting the hydrogen desorption properties of Mg.

In conclusion, we can find that both the hydrogen desorption capacity and rate of Mg are improved by the addition of a certain amount of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloy. With the increase of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ content, the hydrogen desorption kinetics of the composites improves but their capacity decreases at the temperature above 573 K. Specifically, both the hydrogen desorption kinetics and capacity of the composites increase with the enlargement of the (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloy content at the temperature below 573 K.

The JMAK (Johnson–Mehl–Avrami–Kolmogorov) model is used to express the hydrogen sorption kinetics (see eqn (1)):\[ \ln[-\ln(1-\alpha)] = \eta \ln k + \eta \ln t \] where $k$ is the reaction rate constant, $\eta$ is the Avrami exponent of reaction order, and $\alpha$ is the fraction transformed at time $t$. For each temperature, the slope $\eta$ and the intercept $\eta \ln(k)$ can be obtained from the plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln(t)$.

Then, the Arrhenius equation is used to calculate the hydrogenation activation energy: \[ k = A \exp(-E_a/RT) \] where $R$ is the gas constant (8.314472 J mol$^{-1}$ K$^{-1}$), $T$ represents the absolute temperature, $E_a$ is the activation energy, $k$ is the rate constant and $A$ is the pre-exponential factor, a constant. The hydrogenation activation energy of the ball milled Mg UFPs calculated from Fig. 9a is 81.71 kJ mol$^{-1}$, much smaller than Mg UFPs prepared by HPMR without milling of 123.8 kJ mol$^{-1}$,\cite{30} demonstrating the milling process lowers the hydrogenation activation energy. The hydrogenation activation energies of the composite samples also decrease with increasing (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ content. $E_a$ values of the composites with 5, 10, 30 wt% TiMn$_2$ alloy are calculated to be 67.52, 65.80, 60.99 kJ mol$^{-1}$ respectively, see Fig. 9a, much smaller than the ball milled Mg particles. This implies (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ can reduce the hydrogenation activation energy of Mg effectively. They are also smaller than Mg–Nb nanocomposite of 70.9 kJ mol$^{-1}$,\cite{31} indicating the superior catalytic effect of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$. The hydrogenation activation energy of Mg (microsize)–Ti$_{0.98}$Zr$_{0.02}$V$_{0.43}$Fe$_{0.09}$Cr$_{0.03}$Mn$_{1.5}$ composite is 74.22 kJ mol$^{-1}$, higher than those composites in this work.\cite{32} This suggests that the ultrafine size of Mg particles may also help decrease its hydrogenation activation energy.

The dehydrogenation activation energy of the ball milled Mg UFPs calculated from Fig. 9b is 124.75 kJ mol$^{-1}$, smaller than Mg UFPs prepared by HPMR without milling process of 127.7 kJ mol$^{-1}$,\cite{31} demonstrating the milling process lowers the dehydrogenation activation energy. The hydrogenation activation energies of the composite samples also decrease with increasing (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ content. $E_a$ values of the composites with 5, 10, 30 wt% TiMn$_2$ alloy calculated from Fig. 9a are 121.37, 116.68, 77.52 kJ mol$^{-1}$ respectively, smaller than the ball milled Mg particles of 124.75 kJ mol$^{-1}$ (see Fig. 9b). This implies adding (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ can reduce the dehydrogenation activation energy of Mg effectively. The dehydrogenation activation energy of the composite with 30 wt% TiMn$_2$ alloy is lower than that of the Mg–7 at% Al composite of 105.5 kJ mol$^{-1}$ (ref. 30) and the Mg–Nb nanocomposite of 86.4 kJ mol$^{-1}$,\cite{31} demonstrating the superior catalytic effect of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$. Because of the absence of d-electrons orbital, Mg does not have sufficient ability to dissociate hydrogen molecules without catalytic additives. In this work, (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ particles make it easier for H$_2$ molecules to be split into hydrogen atoms through facilitating the dissociation of hydrogen gas molecules during the hydrogenation process.\cite{33} When the dehydrogenation begins, some hydrogen atoms will be released from the MgH$_2$ at the interface of MgH$_2$/ (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ in priority because of destabilization of Mg–H bond by the TiMn$_2$ alloy.\cite{34} As we can see in

\[ \begin{align*}
\text{Fig. 9 } & \text{ Plots of } \ln k \text{ vs. } 1000/T \text{ for the hydrogenation (a) and dehydrogenation (b) of the Mg–x wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ (x = 0, 5, 10, 30) composites.}
\end{align*} \]
Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ does not absorb hydrogen at the testing temperature above 423 K. Hydrogen atoms will therefore be recombined and released in the form of hydrogen molecules immediately once they are generated at the interface. The reduction of H$_2$ accelerates the reaction: MgH$_2$ = Mg + H$_2$, thus the dehydrogenation kinetics will be enhanced. Additionally, the interfaces at the (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$/MgH$_2$ boundaries with high interfacial energy can act as fast hydrogen diffusion paths to accelerate the hydrogen desorption process of MgH$_2$.

Mg–30 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite was selected to evaluate the thermodynamic effects of the (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloy on Mg. The PCT curves of the hydrogen absorption/desorption at 623, 648, and 673 K are plotted in Fig. 10a. Since the (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ does not absorb hydrogen at the testing temperatures, only one flat plateau is detected for each absorption/desorption process as a result of the transformation between Mg and MgH$_2$ at each temperature. The hydrogen equilibrium pressures of the desorption plateaus are 1.45 MPa at 673 K, 0.84 MPa at 648 K, and 0.52 MPa at 623 K. By plotting the logarithm of the equilibrium pressures ln($P$) against the inverse temperature 1000/$T$ and drawing the fitting line according to these plots, the Van’t Hoff equation for absorption is determined as $ln(P) = -9.162/T + 16.361$. The formation enthalpy ($\Delta H_f$) calculated accordingly for the Mg–30 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite is $-76.16 \text{ kJ mol}^{-1}$, which is comparable to the reported enthalpy value for MgH$_2$ ($-75 \text{ kJ mol}^{-1}$). The hydrogen equilibrium pressures of the desorption plateaus are 1.45 MPa at 673 K, 0.84 MPa at 648 K, and 0.48 MPa at 623 K. The Van’t Hoff equation for desorption is $ln(P) = -9.2674/T + 16.439$. The decomposition enthalpy ($\Delta H_d$) for the Mg–30 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite is evaluated to be 77.05 kJ mol$^{-1}$. Thus, the addition of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ does not apparently change the thermodynamics of hydrogenation and dehydrogenation of Mg. The high hydrogen storage capacity and the enhanced hydrogen sorption kinetics are due to the catalytic effect of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloys and the ultrafine size of Mg.

**Fig. 10** P–C isotherm curves at 623, 648, and 673 K (a) and Van’t Hoff plots (b) for the Mg–30 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite.

Conclusions

The Mg–x wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ (x = 0, 5, 10, 30) composites have been successfully prepared by ball milling. The (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ particles are homogeneously distributed on the surface or embedded in the Mg UFPs. Adding (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ alloy contributes to the enhanced hydrogen storage capacities and kinetics. Mg–5 wt% (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ composite can uptake 6.00 wt% H$_2$ within 60 min at 523 K. It can release 6.0 wt% H$_2$ within 15 min at 623 K. Both the hydrogen absorption and desorption kinetics of the composites improve when the content of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ grows. $E_a$ values of the composites with 0, 5, 10, 30 wt% TiMn$_2$ alloy for hydrogenation and dehydrogenation are 81.71, 67.52, 65.80, 60.99 kJ mol$^{-1}$ and 124.75, 121.37, 116.68, 77.25 kJ mol$^{-1}$, respectively. The ultrafine size of Mg and the catalytic effect of (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_{1.2}$Cr$_{0.6}$V$_{0.1}$Cu$_{0.1}$ particles give rise to the improved hydrogen storage capacities and kinetics.

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