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Enhancement of Destabilization and Reactivity of Mg Hydride Embedded in Immiscible Ti Matrix by Addition of Cr: Pd-free Destabilized Mg Hydride

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ABSTRACT: Nanometer-sized Mg hydride clusters may form in a self-organized way by the hydrogenation of a non-equilibrium Mg-Ti alloy. Here the Mg hydride is destabilized by the interface energy between the two metal hydrides. To obtain an even more destabilized Mg hydride, we increased the interface energy by the addition of Cr which is immiscible with Mg as Ti. Indeed, Mg layers surrounded by Ti-Cr layers show hydrogen plateau pressures higher than when Mg is surrounded by Ti. Destabilization of Mg hydride is also observed in hydrogenated Mg-Ti-Cr thin film alloys resulting in hydrogenation plateaus flatter and at higher pressures than in hydrogenated Mg-Ti thin film alloys. Our results suggest that by screening alloys on the basis of their immiscibility with Mg, we can tune the thermodynamics and kinetics of hydrogen

absorption and desorption in Mg-H. This concept paves the way for the development of lightweight and cheap Mg-based functional materials in the metal-hydrogen system.

INTRODUCTION

Metal hydrides have a number of properties that may be utilized to promote the use of hydrogen as an energy carrier. Metal hydrides with a high hydrogen permeability can be applied as membranes for hydrogen separation, while the optical changes occurring in metal thin films upon hydrogenation can be used for hydrogen sensing. Even better known is the fact that the high volumetric density of hydrogen makes metal hydrides an attractive option to store energy. The applicability of metal hydrides for storage applications depends on its affinity to hydrogen which determines the equilibrium pressure for (de-)hydrogenation. One of the most attractive hydride forming metals is Mg because of its light weight and low material costs. However, the Mg-H system has thermodynamic and kinetic limitations associated with hydrogen absorption and desorption processes: the high stability of the MgH_2 phase, the slow diffusion of hydrogen in Mg and MgH_2 and the poor dissociation kinetics of the hydrogen molecule on the Mg surface at moderate temperatures and pressures.

A possible way to destabilize MgH_2 and shorten the hydrogen diffusion length is to reduce the size of the Mg units. A multilayer stack of immiscible Mg/Ti with a typical layer thickness below 10 nm revealed that MgH_2 is destabilized by the effect of the interface energy difference $\Delta\gamma$ between Mg/TiH_2 and MgH_2/TiH_2 upon hydrogenation.[1] We have also demonstrated that nanometer-sized MgH_2 clusters embedded in a TiH_2 matrix are formed by hydrogenation of Ti-rich Mg_xTi_{1-x} ($x < 0.4$) thin films, again resulting in an interface energy induced destabilization of

MgH_2.[2] In these experiments the surface of Mg is covered by a Pd catalyst layer to promote hydrogen dissociation and protect the films against oxidation.[3] To prevent the reaction between Mg and Pd a Ti interface layer is used.

In the present work, we show that the destabilization of MgH_2 can be drastically improved by the addition of Cr. Cr is immiscible with Mg and miscible with Ti.[4] The enthalpy for mixing and interface formation with Mg are 24 and 107 kJ mol^{-1} for Cr, which is higher than for Ti (16 and 67 kJ mol^{-1},[5] respectively). Hence, Cr will selectively mix with the Ti domain. Indeed Ti-Cr is dispersed in Mg matrix in Mg-rich Mg-Ti-Cr thin films.[6] Cr is also a non-hydride forming element under moderate conditions while Mg and Ti are hydride forming ones. We suggest that the $\Delta\gamma$ upon hydrogenation of Mg is changed by the addition of Cr. In case of increasing $\Delta\gamma$, nanometer-sized MgH_2 will be more destabilized. Moreover, we expect Cr to catalyze the hydrogen absorption since $TiCr_2$-based intermetallic compounds with a Laves-type structure and Ti-V-Cr solid solutions with a body centered cubic structure readily absorb hydrogen at moderate temperatures.[7] This would enable the Mg-Ti-Cr system to become a bulk hydrogen storage system with attractive thermodynamic and kinetic properties.

EXPERIMENTAL

In order to prove our concept we prepared three series of Mg-Ti-Cr ternary thin films: (1) to prove the increase in $\Delta\gamma$ and the resulting destabilization of MgH_2 we deposited multilayer stacks of $Mg/Ti_{0.33}Cr_{0.67}$ with various Mg thicknesses; (2) to investigate the destabilization of nanometer-sized MgH_2 clusters in Ti-Cr-based matrix we prepared compositional gradient $Mg_x(Ti_{1-y}Cr_y)_{1-x}$ ($x = 0.35$ and 0.50, while $0.55 \leq y \leq 0.75$) thin films; (3) to verify the catalytic effect of Cr we deposited homogeneous $Mg_{0.35}(Ti_{0.33}Cr_{0.67})_{0.65}$ ternary thin films without the Pd cap-layer. All thin films and multilayers were deposited at room temperature on quartz substrates under an argon atmosphere in an ultrahigh vacuum RF/DC magnetron co-sputtering system with off-centered sources. The hydrogenation and dehydrogenation properties of our thin films were evaluated by means of an optical technique called hydrogenography which allows to measure the P (pressure)-T (optical transmission) isotherms.[8-10] According to Lambert-Beer the relation $\ln(T/T_0)$ is proportional to $C_H d$, where T_0 is the initial transmission, C_H is the hydrogen content in the film, and d is the film thickness.[11] The detailed procedures were described in previous reports.[1,2]

RESULTS AND DISCUSSION

Effect of addition of Cr to Ti on destabilization of Mg hydride

The multilayer stacks consist of three Mg layers with a thickness of 10, 5 and 2 nm. Every Mg layer is surrounded by two 5 nm layers of $Ti_{0.33}Cr_{0.67}$ or Ti. Both types of stacks are covered by 10 nm layer of Pd, as shown in **Figure 1**a. The P-T isotherms of the multilayer stacks measured at 423 K are shown in Figure 1b. Before the actual measurements three hydrogen absorption and desorption cycles were applied to obtain a stabilized structure and reproducible response. At the applied conditions ($P = 1 - 10^5$ Pa and T (temperature) = 423 K) Ti forms a hydride phase, while Pd and Cr form a hydrogen solid solution phase. The optical change of $\ln(T/T_0)$ is mainly due to the hydrogenation and dehydrogenation of the Mg layers, corresponding to the transformation between the metallic Mg and transparent MgH_2 phases. The absorption plateau pressure is higher than the desorption one because of the effect of plastic deformation by hydrogenation as reported by Mooij et al.[1] Clearly, we observe steps in the absorption and desorption plateau regions which are attributed to the coexistence of the two phases. Mooij et al. have shown that the plateau pressure increases with a decreasing Mg thickness of *d* from 10 down to 1.5 nm in the Mg/Ti multilayer stack.[1] In the present work, as shown in Figure 1b, the plateau pressure similarly increases with decreasing *d* from 10 down to 2 nm. The highest plateau pressure for *d* = 2 nm in the Mg/$Ti_{0.33}Cr_{0.67}$ multilayer stack looks slightly higher than that of Mg/Ti in both absorption and desorption processes. The increase in the plateau pressure of the Mg layers as function of *d* in the Mg/Ti multilayer stack is described by eq 1.[1]

$$\ln\left(\frac{P_{nano}}{P_{thick}}\right) = \frac{2V\Delta\gamma}{RTd} \qquad (1)$$

Here, the change in interface energy between Mg and TiH_2 upon hydrogenation is $\Delta\gamma$. The symbols of P_{nano} and P_{thick} are the plateau pressures of Mg for a nanometer-sized thin film, and a thick film of at least 50 nm, respectively. The symbol V is the molar volume of Mg, R the gas constant and T the temperature. By plotting P_{nano} versus the inverse of d, the slope gives the value of $\Delta\gamma$ when the plot shows a linear dependence. The calculated value of $\Delta\gamma$ for the Mg/Ti multilayer stack is $\Delta\gamma_{\text{ab}} = 0.44$ J m^{-2} for the absorption process and $\Delta\gamma_{\text{de}} = 0.17$ J m^{-2} for the desorption process (Figure 1c). These values have a probability of errors because the present plot consists of only three points but agree very well with the ones as reported by Mooij et al.[1] The value of $\Delta\gamma$ for the Mg/$Ti_{0.33}Cr_{0.67}$ multilayer stack is calculated to be $\Delta\gamma_{\text{ab}} = 0.54$ J m^{-2} and $\Delta\gamma_{\text{de}} = 0.20$ J m^{-2}, which are ~20% higher than those for the Mg/Ti multilayer stack. These results suggest that the addition of Cr to Ti is effective to destabilize MgH_2 by increasing $\Delta\gamma$.

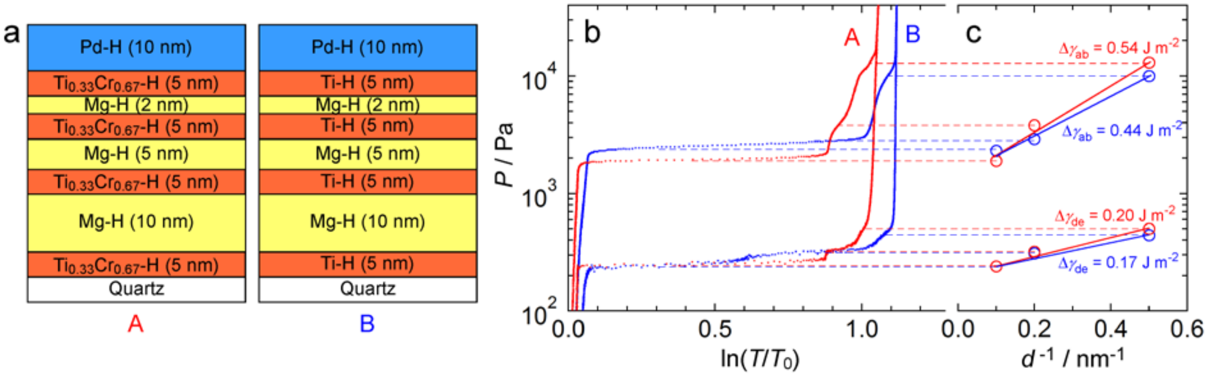

Figure 1. (a) A schematic representation of Mg/$Ti_{0.33}Cr_{0.67}$ (red A) and Mg/Ti (blue B) multilayer geometry. (b) *P-T* isotherms measured at 423 K where the transition between Mg and MgH_2 as a function of the thicknesses of 10, 5 and 2 nm. (c) Plateau pressures versus inverse layer thickness and $\Delta\gamma$ for the absorption and desorption processes calculated from the slope of the linear fit. The errors are smaller than the symbols.

Enhancement of destabilization of Mg hydride in Mg-Ti-Cr

Since both Ti and Cr are immiscible with Mg, both in the hydrogenated and dehydrogenated states, it is fascinating whether a similar destabilization would occur in a homogeneously mixed layer. **Figure 2** shows schematically the structural change that might be induced by hydrogenation of Mg-Ti-Cr. We expect that Ti, Cr and Mg form a non-equilibrium solid solution when deposited by magnetron co-sputtering. As we have reported for the Ti-rich Mg_xTi_{1-x}-H_2 systems,[2] hydrogenation forms MgH_2 domains which are coherently embedded in an immiscible TiH_2 matrix with a face centered cubic (FCC) structure, while bulk MgH_2 has a body centered tetragonal (BCT) structure. Hence, the hydrogenation of Mg-Ti-Cr leads to form Mg domains embedded in a Ti-Cr-based matrix which increases the value of Δγ. The structure of Mg-Ti-Cr after hydrogenation is assumed to be an FCC structure in Figure 2. However, Mg domains might have a different structure rather than an FCC structure if a Ti-Cr based matrix has, for instance, a C15-type cubic Laves phase structure. Indeed, it has been reported that body centered cubic (BCC) Mg[12] and orthorhombic MgH_2 [13,14] are formed in the Mg/Nb multilayer stack, resulting in a lower stability of Mg and MgH_2. To prove this effect of the addition of Cr we measured the *P*-*T* isotherms for $Mg_x(Ti_{1-y}Cr_y)_{1-x}$-H_2 ($x = 0.35$ and 0.50, while $0.55 \leq y \leq 0.75$) systems at 393 K (**Figure 3**a and b) in a 60 nm compositional gradient $Mg_x(Ti_{1-y}Cr_y)_{1-x}$ thin film. The film is surrounded by two thin Ti layers to protect it against a reaction with the 10 nm Pd catalyst layer. For comparison we included Figure 3c which shows the isotherms for the Mg_xTi_{1-x}-H_2 ($0.16 \leq x \leq 0.53$) system at the same temperature measured previously.[2] In all cases, three hydrogen absorption and desorption cycles were performed before the actual measurements were done.

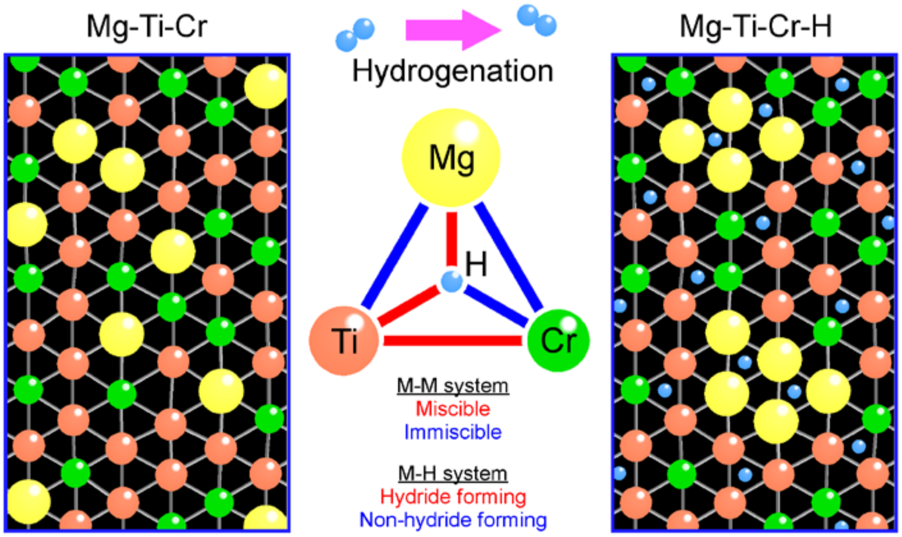

Figure 2. A schematic structural change in the first hydrogenation of Mg-Ti-Cr. Mg, Ti and Cr form a non-equilibrium solid solution which is deposited by means of magnetron co-sputtering. Mg domains are self-organized by hydrogenation on the basis of the immiscibility of Mg-Ti and Mg-Cr and the miscibility of Ti-Cr.

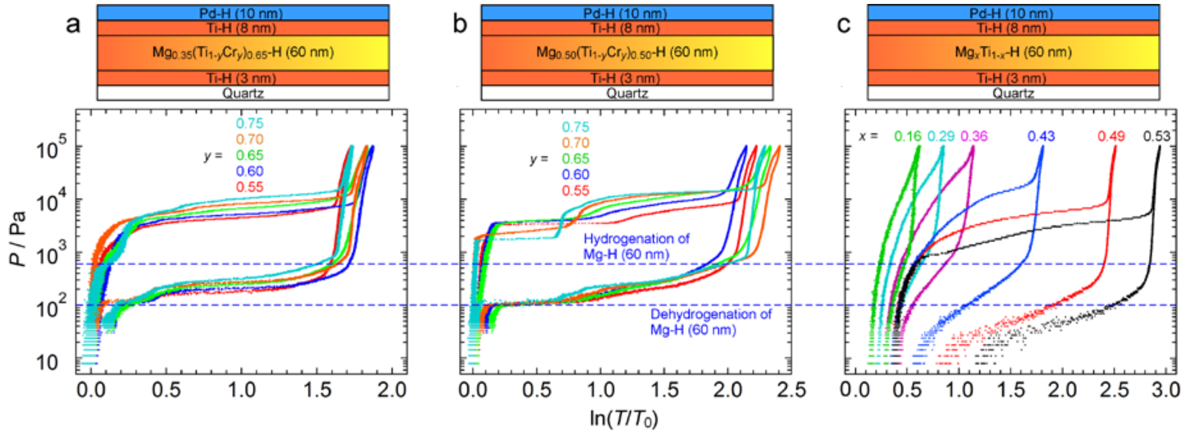

Figure 3. Schematic representations of multilayer geometry and *P*-*T* isotherms of the (a) $Mg_{0.35}(Ti_{1-y}Cr_y)_{0.65}$-$H_2$, (b) $Mg_{0.50}(Ti_{1-y}Cr_y)_{0.50}$-$H_2$ ($0.55 \leq y \leq 0.75$) and (c) Mg_xTi_{1-x}-H_2 ($0.16 \leq x \leq 0.53$) systems measured at 393 K. The dotted lines indicate the hydrogenation and dehydrogenation pressures for 60 nm of Mg.

We find both for $x = 0.35$ and 0.50 absorption and desorption isotherms that show large plateau regions. Given the large optical contrast we attribute these plateaus to the coexistence of the metal and hydride phases of the Mg domains in $Mg_x(Ti_{1-y}Cr_y)_{1-x}$-H layer. The plateau pressures are slightly higher pressures than in 60 nm of Mg.[2] For $x = 0.35$ shown in Figure 3a, the plateau pressures in the absorption and desorption processes at $y = 0.55$ are 4.5×10^3 and 1.9×10^2 Pa, respectively. Those increase as function of increasing Cr content: 1.1×10^4 and 3.2×10^2 Pa at $y = 0.75$. For $x = 0.50$ shown in Figure 3b, the absorption and desorption isotherms show two plateau regions (the lower region of $\ln(T/T_0) < 0.7$ and the upper one of $\ln(T/T_0) > 1.0$, respectively). The plateau pressure for the upper region is equivalent to that for $x = 0.35$.

Previously we explained the increase in the plateau pressure in the Mg_xTi_{1-x}-H_2 system shown in Figure 3c in terms of spherical Mg domains embedded in a TiH_2 matrix as expressed by eq 2.[2]

$$\ln\left(\frac{P_{nano}}{P_{thick}}\right) = \frac{3V\Delta\gamma}{RTr} \qquad (2)$$

The symbol r is the radius of Mg domains. We derived a minimum radius of $r_{\min}$ = ~1 nm of Mg clusters in Ti-rich Mg_xTi_{1-x}-H for compositions with $x < 0.4$.[2] The sloping nature of the plateaus was explained to be due to the various tetrahedral Mg_jTi_{4-j} ($0 \leq j \leq 4$) coordinations of hydrogen, where hydrogen is stabilized by the Ti coordination.[15]

The isotherms in the $Mg_{0.35}(Ti_{1-y}Cr_y)_{0.65}$-$H_2$ system shown in Figure 3a have flatter absorption and desorption plateau regions with higher plateau pressures than in the Mg_xTi_{1-x}-H_2 system (Figure 3c). This suggests that the addition of Cr, which is a non-hydride forming element, lowers the thermodynamic effect of the tetrahedral sites by the higher Ti coordination of Mg_jTi_{4-j}, resulting in the flatter and higher plateau. The addition of Cr also contributes to the increase in $\Delta\gamma$, which increases the plateau pressure, assuming that the r is hardly changed by Cr. The enthalpy for hydride dissociation of MgH_2 in $Mg_{0.35}(Ti_{0.25}Cr_{0.75})_{0.65}$-H is estimated to be –68 – –71 kJ mol^{-1}-H_2 (–74.3 kJ mol^{-1}-H_2 for bulk MgH_2[16]). When we increase the Mg fraction we observe a double plateau (Figure 3b). We attribute the upper plateau region in the $Mg_{0.50}(Ti_{1-y}Cr_y)_{0.50}$-$H_2$ system to the hydrogenation and dehydrogenation of nanometer-sized Mg domains, which are observed also in the $Mg_{0.35}(Ti_{1-y}Cr_y)_{0.65}$-$H_2$ system. The approximate volume fractions of Mg in $Mg_{0.35}(Ti_{0.35}Cr_{0.65})_{0.65}$ and $Mg_{0.50}(Ti_{0.35}Cr_{0.65})_{0.50}$ are estimated to be ~48% and ~63% from the atomic weight and density of Mg, Ti and Cr, respectively. Thus, a part of the Mg in $Mg_{0.50}(Ti_{1-y}Cr_y)_{0.50}$-H layer is no longer present in the form of destabilized nanometer-sized clusters, but rather in the form of MgH_2, corresponding to the lower plateau region which has close plateau pressures for 60 nm of Mg as dotted lines.

Catalytic effect of Cr

To investigate the catalytic effect of Cr the hydrogen absorption curves of three homogeneous $Mg_{0.35}(Ti_{0.33}Cr_{0.67})_{0.65}$ thin films were measured under a hydrogen pressure of 1 MPa at 423 K. The three films are 60 nm layer of $Mg_{0.35}(Ti_{0.33}Cr_{0.67})_{0.65}$ deposited on 3 nm layer of Ti. One of the films is covered by 8 nm layer of Ti and 10 nm layer of Pd and another by 8 nm layer of Cr, as shown in **Figure 4**a. The absorption curves shown in Figure 4b correspond to the first hydrogenation after exposing the deposited thin films to air. The film covered by Pd layer is hydrogenated within 200 s (Figure 4c), which indicates the catalytic effect of Pd for hydrogen absorption. Hydrogenation of the other two films takes much longer time (~2×10^5 s). Nevertheless, this result indicates that Cr catalyzes the hydrogen absorption because thin films consisting only of Mg and Ti do not react with hydrogen under the same condition.

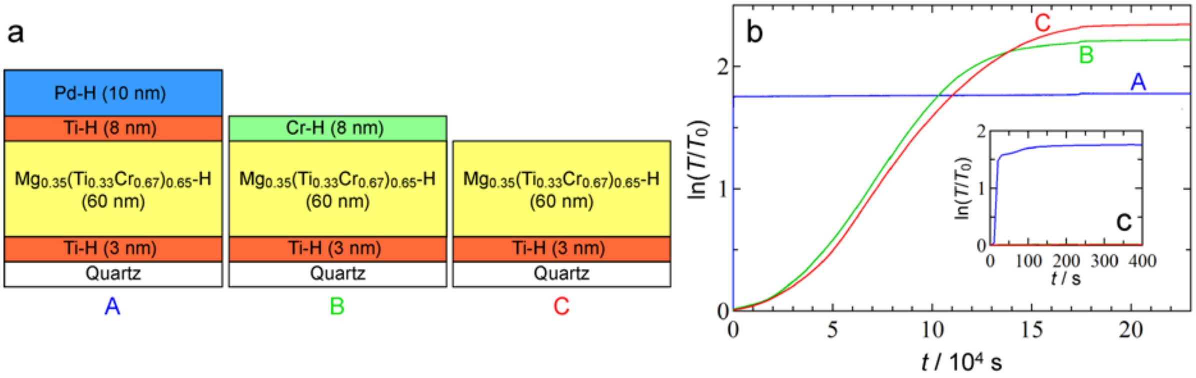

Figure 4. (a) A schematic representation of multilayer geometry for $Mg_{0.35}(Ti_{0.33}Cr_{0.67})_{0.65}$ covered by Ti and Pd layers (blue A), that covered by Cr layer (green B) and that without covered layer (red C). (b) Optical transmission versus time corresponding to hydrogen absorption curves measured under 1 MPa-H_2 at 423 K ((c) in the region of $t \leq 400$ s).

CONCLUSION

We have shown the possibility that nanometer-sized metal hydride clusters embedded in an immiscible matrix form by self-organization during hydrogenation. By changing the nature of the matrix we are able to tailor the thermodynamics of the hydride through the interface energy. The addition of Cr, which is immiscible with Mg as Ti, is effective to destabilize MgH_2 clusters more than Ti alone. In the previous study we have successfully destabilized MgH_2 clusters in Ti-rich Mg_xTi_{1-x}-H but those samples needed a Pd cap-layer to catalyze the hydrogen absorption. Here, we have confirmed the catalytic effect of Cr for the hydrogen absorption. The application of Pd-free destabilized MgH_2 embedded in an immiscible matrix can be extended to a bulk scale; membranes for hydrogen separation and powders for hydrogen storage, etc. Synthesizing bulk of non-equilibrium Mg-based alloys and self-organizing MgH_2 clusters by hydrogenation are in progress, which offers attractive new possibilities on the metal-hydrogen system.

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REFERENCES

1. Mooij, L. P. A.; Baldi, A.; Boelsma, C.; Shen, K.; Wagemaker, M.; Pivak, Y.; Schreuders, H.; Griessen, R.; Dam, B. Interface Energy Controlled Thermodynamics of Nanoscale Metal Hydrides. *Adv. Energy Mater.* **2011**, *1*, 754-758.

2. Asano, K.; Westerwaal, R. J.; Anastasopol, A.; Mooij, L. P. A.; Boelsma, C.; Ngene, P.; Schreuders, H.; Eijt, S. W. H.; Dam, B. Destabilization of Mg Hydride by Self-Organized Nanoclusters in the Immiscible Mg-Ti System. *J. Phys. Chem. C* **2015**, *119*, 12157-12164.

3. Baldi, A.; Gonzalez-Silveira, M.; Palmisano, V.; Dam, B.; Griessen, R. Destabilization of the Mg-H System through Elastic Constraints. *Phys. Rev. Lett.* **2009**, *102*, 226102.

4. Phase Diagrams of Binary Magnesium Alloys; Nayeb-Hashemi, A. A.; Clark, J. B., Eds.; ASM International, 1988; p 142.

5. Cohesion in metals: transition metal alloys; de Boer, F. R.; Boom,R.; Mattens, W. C. M.; Miedema, A. R;. Niessen, A. K.; North-Holland Physics 1988

6. Zahiri, B.; Amirkhiz, B. S.; Mitlin, D. Hydrogen storage cycling of MgH_2 thin film nanocomposites catalyzed by bimetallic Cr Ti. *Appl. Phys. Lett.* **2010**, *97*, 083106.

7. Akiba, E.; Iba, H. Hydrogen absorption by Laves phase related BCC solid solution. *Intermetallics* **1998**, *6*, 461-470.

8. Gremaud, R.; Broedersz, C. P.; Borsa, D. M.; Borgschulte, A.; Mauron, P.; Schreuders, H.; Rector, J. H.; Dam, B.; Griessen, R. Hydrogenography: An Optical Combinatorial Method to Find New Light-Weight Hydrogen-Storage Materials. *Adv. Mater.* **2007**, *19*, 2813-2817.

9. Gremaud, R.; Slaman, M.; Schreuders, H.; Dam, B.; Griessen, R. An Optical Method to Determine the Thermodynamics of Hydrogen Absorption and Desorption in Metals. *Appl. Phys. Lett.* **2007**, *91*, 231916.

10. Westerwaal, R. J.; den Besten, C., Slaman, M.; Dam, B.; Nanu, D. E.; Böttger, A. J.; Haije, W.G. High Throughput Screening of Pd-alloys for H_2 Separation Membranes Studied by Hydrogenography and CVM. *Int. J. Hydrogen Energy* **2011**, *36*, 1074-1082.

11. Borgschulte, A.; Westerwaal, R. J.; Rector, J. H.; Dam, B.; Griessen, R. Hydrogen Sorption Mechanism of Oxidized Nickel Clusters. *Appl. Phys. Lett.* **2004**, *85*, 4884.

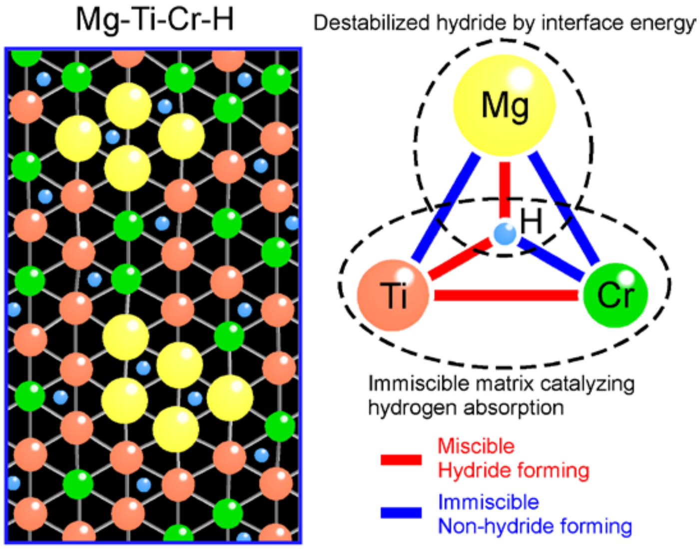
12. Junkaew, A.; Ham, B.; Zhang, X.; Talapatra, A.; Arróyave, A. Stabilization of bcc Mg in Thin Films at Ambient Pressure: Experimental Evidence and *ab initio* Calculations. *Mater. Res. Lett.* **2013**, *1*, 161-167.

13. Kumar, A.; Beyerlein, I. J.; Wang, J. First-principles study of the structure of Mg/Nb multilayers. *Appl. Phys. Lett.* **2014**, *105*, 071602.

14. Ham, B.; Junkaew, A.; Arroyave, R.; Chen, J.; Wang, H.; Wang, P.; Majewski, J.; Park, J.; Zhou, H.-C.; Arvapally, R. K.; Kaipa, U.; Omary, M. A.; Zhang, X. Y.; Ren, Y.; Zhang, X. Hydrogen sorption in orthorhombic Mg hydride at ultra-low temperature. *Int. J. Hydrogen Energy* **2013**, *38*, 8328-8341.

15. Gremaud, R.; Baldi, A.; Gonzalez-Silveira, M.; Dam, B.; Griessen, R. Chemical Short-range Order and Lattice Deformations in $Mg_yTi_{1-y}H_x$ Thin Films Probed by Hydrogenography. *Phys. Rev. B* **2008**, *77*, 144204.

16. Stampfer, J.; Holley, C.; Suttle, J.; The Magnesium-Hydrogen System. *J Am. Chem. Soc.* **1960**, *82*, 3504-3508.


Mg-Ti-Cr-H
Destabilized hydride by interface energy
Mg
H
Ti
Cr
Immiscible matrix catalyzing hydrogen absorption
Miscible
Hydride forming
Immiscible
Non-hydride forming

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