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Mesoscale Modeling of Kinetic Phase Behaviors in Mg-B-H (Subcontract Report)

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FY17 Annual Report for Subcontract to University of Michigan Subcontract B611071 for “Improving the Kinetics and Thermodynamics of $Mg(BH_4)_2$ for Hydrogen Storage”

Title: Mesoscale modeling of kinetic phase behaviors in Mg-B-H

Personnel: Dr. Hui-Chia Yu, Prof. Katsuyo Thornton (University of Michigan); PI: Dr. Brandon Wood (LLNL)

Purpose: Provide phase-field model for studying kinetics of phase evolution in Mg-B-H system

Period of work: 10/2016 to 9/2017

Work location: University of Michigan

Project description:
Storage of hydrogen on board vehicles is one of the critical enabling technologies for creating hydrogen-fueled transportation systems that can reduce oil dependency and mitigate the long-term effects of fossil fuels on climate change. Stakeholders in developing hydrogen infrastructure are currently focused on high-pressure storage at 350 bar and 700 bar, in part because no viable solid-phase storage material has emerged. Nevertheless, solid-state materials, including high-density hydrides, remain of interest because of their unique potential to meet all DOE targets and deliver hydrogen at lower pressures and higher on-board densities. A successful solution would significantly reduce costs and ensure the economic viability of a U.S. hydrogen infrastructure. The $Mg(BH_4)_2$-MgB_2 system represents a highly promising solution because of its reasonable reaction enthalpy, high intrinsic capacity, and demonstrated reversibility, yet suffers from poor reaction kinetics. This subcontract aims to deliver a phase-field model for the kinetics of the evolution of the relevant phases within the Mg-B-H system during hydrogenation and dehydrogenation. This model will be used within a broader theory, synthesis, and characterization framework to study the properties of geometry-selected nanoparticles of pristine and doped $MgB_2/Mg(BH_4)_2$ with two aims: (1) understand the intrinsic limitations in (de)hydrogenation; (2) devise strategies for improving thermodynamics and kinetics through nanostructuring.

Summary of progress:
In the past year, Dr. Yu and Prof. Thornton continued to develop the model for phase evolution in the Mg-B-H system. They have used their simulations to examine the hypothesis that the irreversible rehydrogenation of MgB_2 is due to the asymmetry in chemical reaction pathways, in which dehydrogenation occurs via a two-step process as described by Eq. (1), while rehydrogenation occurs via a one-step process as described by Eq. (2).

$$MgB_{12}H_{12}+2Mg \rightarrow 6H_2+3MgB_4 \quad \text{and} \quad 3MgB_4+3Mg \rightarrow 6MgB_2 \tag{1}$$

$$6MgB_2+6H_2 \rightarrow MgB_{12}H_{12}+5Mg \tag{2}$$

Their activities of developing the phase field modeling are described below.

- Construct energy landscapes: Dr. Yu and Prof. Thornton have developed a method to render energy landscape as a function of Mg-B-H compositions. This method is similar to the minimal model for ternary phase field approach [1, 2], but with the flexibility to include more than three local energy minima. They focused the modeling on the dynamics and kinetics in the B-rich region (Phase Triangle 3 in Fig. 1(a)) of the composition map, where Eqs. (1) and (2) are involved. Using the *ab initio* calculated free energies of the relevant stoichiometric compounds updated by Kang and Wood, Yu and Thornton constructed a new energy landscape shown in Fig. 1(b), where four local energy minima are set at the compositions corresponding to $MgB_{12}H_{12}$, MgB_4, MgB_2, and Mg, the four stable compounds involved in Eqs. (1) and (2). These four compounds are selected according to the experimental report by H.-W. Li *et al* [3].
- Phase field simulation for dehydrogenation: The simulation for dehydrogenation of $MgB_{12}H_{12}$ was first performed with the new energy landscape, and the result was similar to that in the subcontract report for the last year (2016). The evolution proceeded via two stages. In Stage 1, $MgB_{12}H_{12}$ decomposed to MgB_4 and Mg as described by the first part of Eq. (1). After H is completely

extracted from the particle, the reaction entered Stage 2, where MgB_4 and Mg combined to form MgB_2 as described by the second part of Eq. (1).

- Phase field simulation for hydrogenation:
  <u>Case 1:</u> Yu and Thornton also performed simulations for hydrogenation of MgB_2 particles. For these simulations, a boundary condition of high H chemical potential (equivalent to high H_2 pressure) must be imposed to trigger the reaction. Such a large H potential indicates a large nucleation barrier that must be overcome for the initial insertion of H into MgB_2, which corresponds to the steep gradient on the energy surface along the H axis near the location of MgB_2. Once the hydrogenation starts, H chemical potential outside the particle can be decreased while still continuing the hydrogenation of the particle. Figure 2 shows the simulation results, for which B and Mg mobilities are assumed to be sluggish compared to H mobility, as in the setup of dehydrogenation simulation. As H is inserted into the particle, a core-shell morphology forms, with a layer of non-stoichiometric shell (the composition is approximately MgB_4H_4, shown as the green color) and a core of MgB_2. The reaction pathway directly traverses through Phase Triangle 3 (indicated by the magenta arrows in Figs. 2(b) through 2(d)) because the low B and Mg mobilities hinder separation between these two species to form stoichiometric compounds, such as MgB_4 and metallic Mg.
  <u>Case 2:</u> Another simulation was performed to examine the kinetic effects on the rehydrogenation process, in which the B and Mg mobilities were set to be higher than H mobility (Fig. 3). The boundary condition on the particle surface was kept the same as in the previous case. The result shows a very different morphological evolution from the previous one (Case 1). As shown in Fig. 3(b), a $MgB_{12}H_{12}$ layer form near the particle surface initially as H is inserted into the particle. As hydrogenation proceeds, phases with high Mg concentration emerge from the MgB_2 region. After that, MgB_4 phases (indicated by the yellow color in Fig. 3(c)) form from the MgB_2 region. The Mg phases and MgB_4 phases grow as the MgB_2 region contracts. In the meantime, the MgB_4 phases transform to $MgB_{12}H_{12}$, which can be observed as the expansion of the $MgB_{12}H_{12}$ layer. Eventually, the particle transforms to $MgB_{12}H_{12}$ with Mg inclusions. The evolution qualitatively reverses that during the two-stage dehydrogenation. When the compositions sampled in the particle are plotted on the phase triangle, the results in Figs. 3(b) through 3(d) show the reaction pathways approximately follows that during dehydrogenation. This set of simulations indicate that the key to enhancing rehydrogenation kinetics is to mobilize B and Mg species, such that the composition evolution is allowed to occur via the low-energy pathways for the dehydrogenation process (the blue and green arrows along the edges of Phase Triangle 3 in Fig. 1(b)). Otherwise, rehydrogenation needs to occur via a high-energy pathway traversing across Phase Triangle 3 (the magenta arrow in Fig. 1(b)).
- Phase field simulation for multistep reaction: Yu and Thornton also worked on generalizing the phase-field simulation code to include all the three steps in the dehydrogenation reaction. They constructed three energy landscapes, each of which corresponds to one reaction step as proposed in Ref [3]. The local energy minima of the energy surface for each step are calibrated using the free energies calculated by Kang and Wood. These energy landscapes are shown in Fig. 4, where the energy landscapes for steps 1, 2, and 3 are for temperatures at 290, 350, and 380 °C. A set of phase-field simulation was performed to examine the dehydrogenation process that includes the three reaction steps. A preliminary result is shown in Fig. 5, which shows the conversion of $Mg(BH_4)_2$ to $MgB_{12}H_{12}$ and MgH_2. While the simulation result provided a proof of the feasibility of phase-field simulation for the entire reaction process of dehydrogenation-rehydrogenation cycle. In order to ensure a stable numerical simulation throughout different energy landscapes that exhibit large variations between the energy barriers presented in different energy landscapes, as in our case of the Mg-B-H system, parameter sets for simulations must be deliberately selected or, more precisely, designed. Yu and Thornton have been working on searching a proper set of parameters for further simulation. A full phase-field simulation that covers the multiple reaction steps is underway.

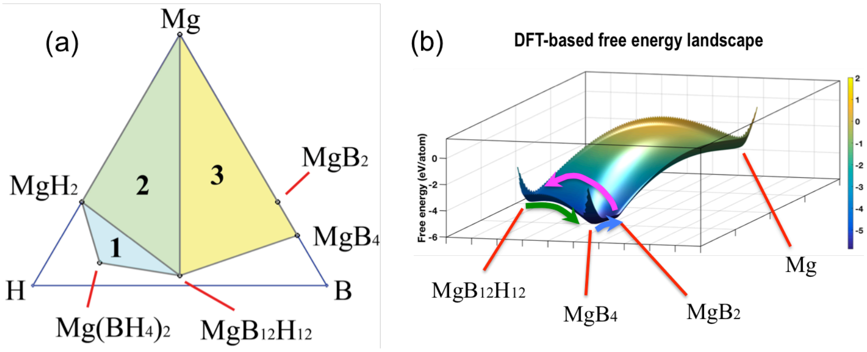

Figure 1. (a) The composition space of the Mg-B-H system. The relevant compounds are grouped into three phase triangles, labeled by 1, 2, and 3. The three phase triangles correspond to the three reaction steps during the dehydrogenation of $Mg(BH_4)_2$. (b) The energy landscape for Phase Triangle 3. The heights of local energy minima are set at the DFT-calculated free energies for the corresponding compounds at 350 °C according to the validated phase diagram.

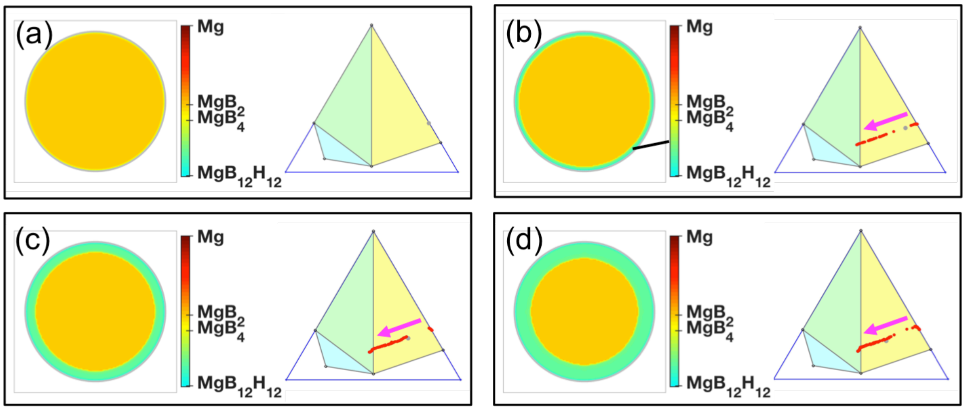

Figure 2: Simulated phase evolution during rehydrogenation of MgB_2 in the case where B and Mg mobilites are much smaller than H mobility (M_H = 1e-2, M_B = 1e-4, and M_{Mg} = 1e-4). The color in the left panel in each subfigure indicates the phase distribution in the particle. The right panel in each subfigure shows the compositions plotted as red markers (sampled every five grid points along the two coordinate axes within the particle) on the phase triangle. The average H fraction in the particle is 0, 0.08, 0.16, 0.225 in (a) through (d), respectively.

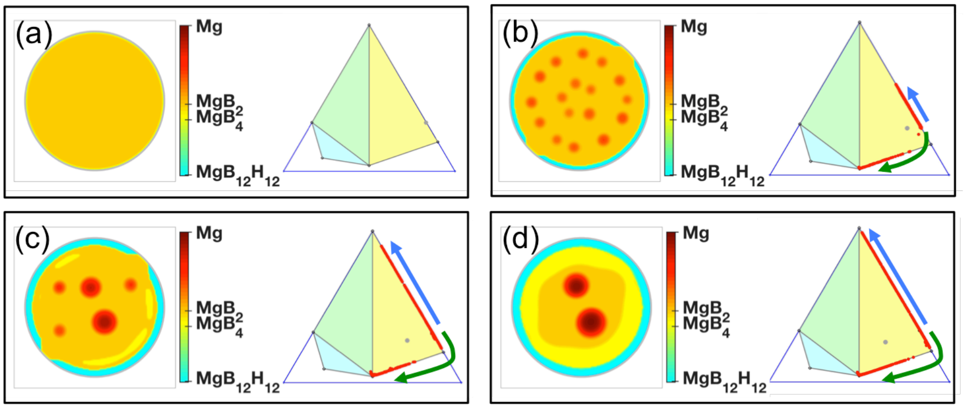

Figure 3: Simulated phase evolution during rehydrogenation of MgB_2 in the case where B and Mg mobilites are larger than H mobility (M_H = 1e-2, M_B = 1e0, and M_{Mg} = 2e-1). The color in the left panel in each subfigure indicates the phase distribution in the particle. The right panel in each subfigure shows the

compositions plotted as red markers (sampled every five grid points along the two coordinate axes within the particle) on the phase triangle. The average H fraction in the particle is 0, 0.08, 0.16, 0.225 in (a) through (d), respectively.

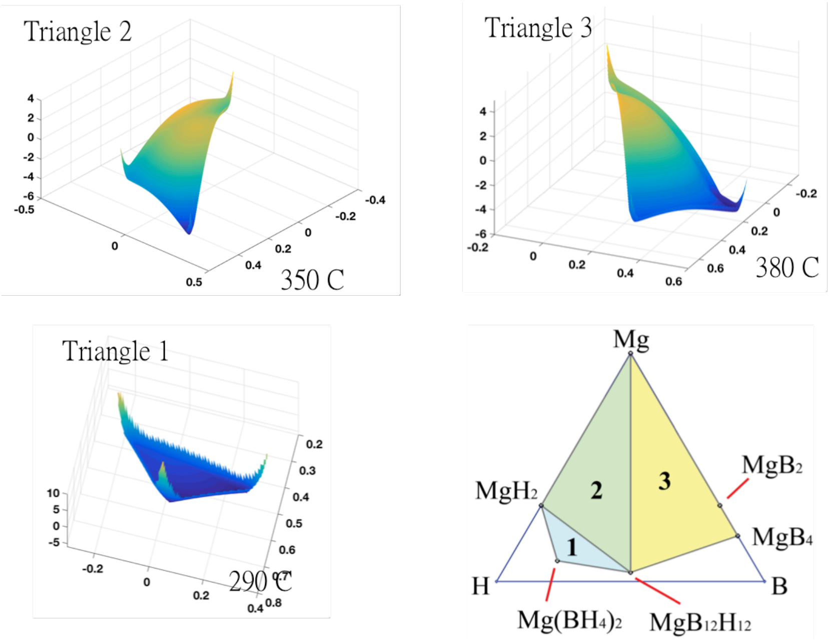

Figure 4: The energy landscapes for the three phase triangles corresponding to the three dehydrogenation reaction steps. The phase triangles are labeled as 1, 2, and 3 on the composition map in the lower right panel. The three energy landscapes are constructed for temperatures at 290, 350, and 380 C, where the energy landscapes are constructed by setting the local minima to be the free energies from atomic calculations at those temperatures.

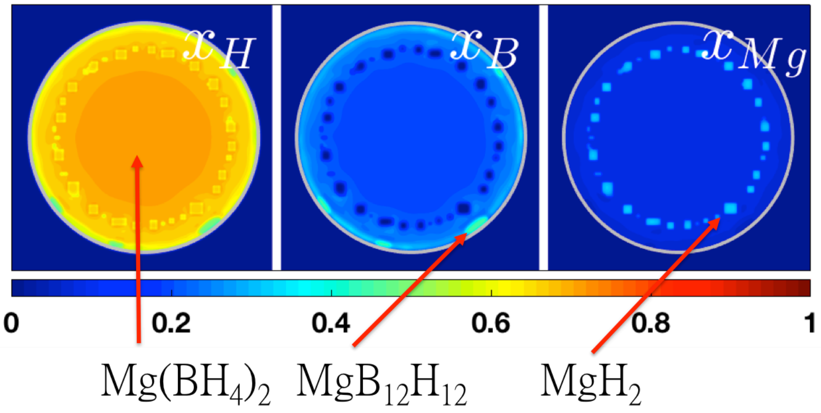

Figure 5: Simulated atomic fractions of H, B, and Mg in a spherical $Mg(BH_4)_2$ particle at the early stage of dehydrogenation, which is in Phase Triangle 1 ($Mg(BH_4)_2$-$MgB_{12}H_{12}$-MgH_2). The majority of the particle is still of $Mg(BH_4)_2$ as indicated by the orange color corresponding to H fraction to be 0.72 on the left panel. There are some $MgB_{12}H_{12}$ phases nucleate on the particle surface, while some MgH_2 phases precipitate in the particle. The square shape of MgH_2 precipitates is from numerical artifact due to inappropriate parameter selection.

References:

[1] R. Rolch and M. Plapp, *Phys Rev E*, **72**, 011602 (2005).
[2] H.-C. Yu, F. Wang, G. G. Amatucci, and K. Thornton, *J Phase Equilib Diff*, **37**, 86 (2016)
[3] H.-W. Li, Y. Yan, S.-I. Orimo, A. Züttel, and C. M. Jensen, *Energies*, **4**, 185 (2011)