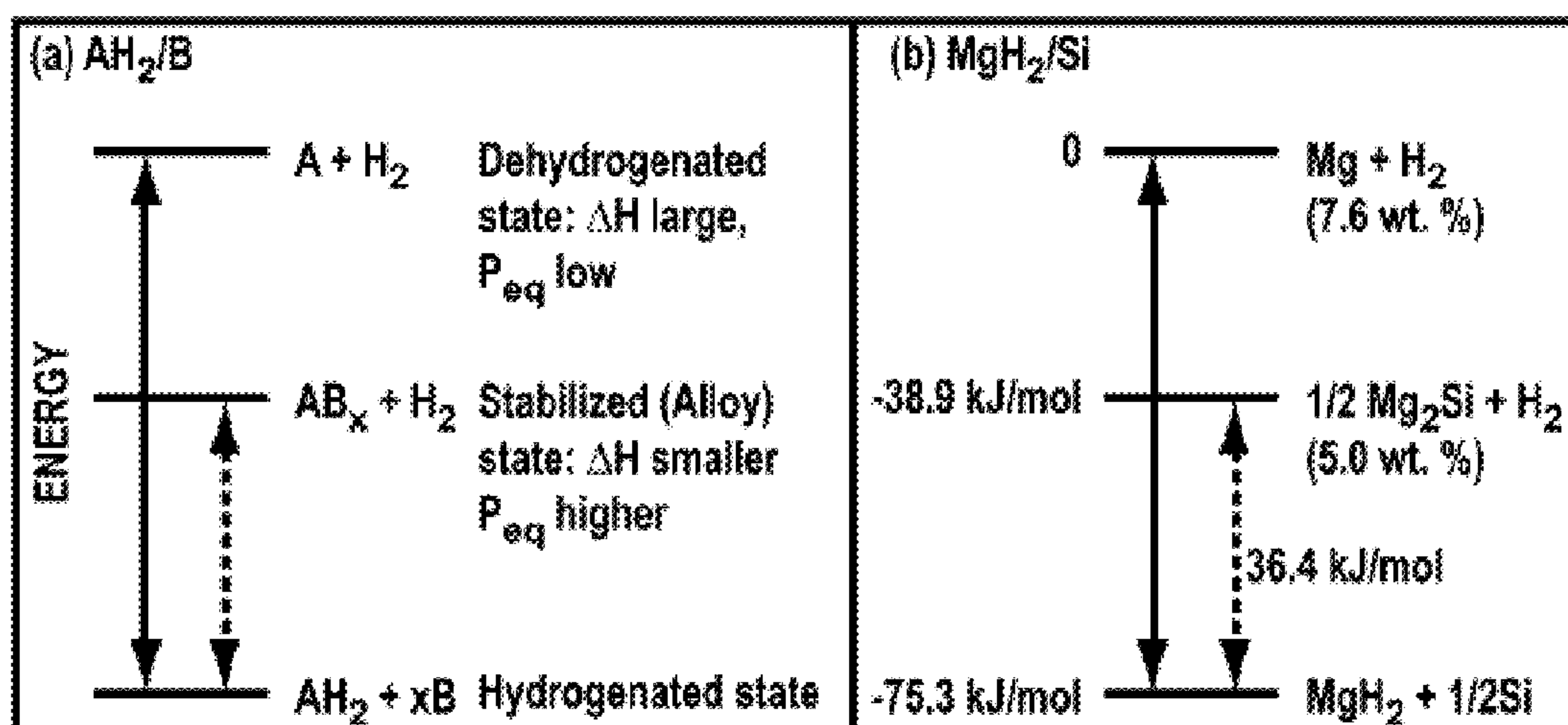


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**Fang et al.**(10) **Pub. No.: US 2011/0091352 A1**(43) **Pub. Date: Apr. 21, 2011**(54) **LIGHT METAL SOLID SOLUTION ALLOYS  
FOR HYDROGEN STORAGE****Publication Classification**(76) Inventors: **Zhigang Z. Fang**, Salt Lake City,  
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Lake City, UT (US); **Young Joon  
Choi**, Salt Lake City, UT (US)(51) **Int. Cl.**  
**C22C 28/00** (2006.01)  
**C22C 1/00** (2006.01)(52) **U.S. Cl. .... 420/591**(21) Appl. No.: **12/757,852**(22) Filed: **Apr. 9, 2010****Related U.S. Application Data**(60) Provisional application No. 61/167,990, filed on Apr.  
9, 2009.(57) **ABSTRACT**

A light metal solid solution alloy for reversible hydrogen storage can include a light metal solid solution alloy of  $M_1$  and  $M_2$ .  $M_1$  and  $M_2$  are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si. Furthermore, the starting materials and formation conditions are chosen such that the resulting alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.



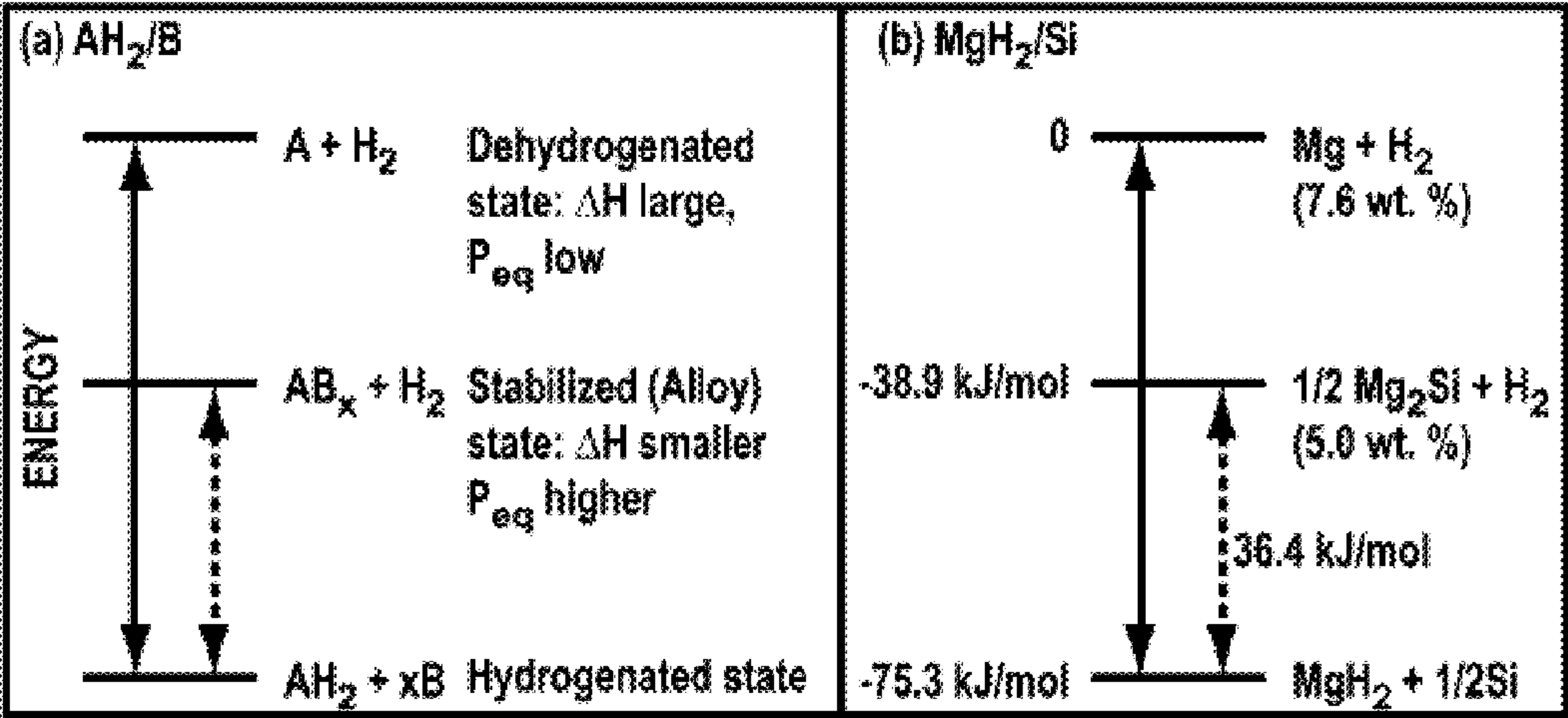


FIG. 1

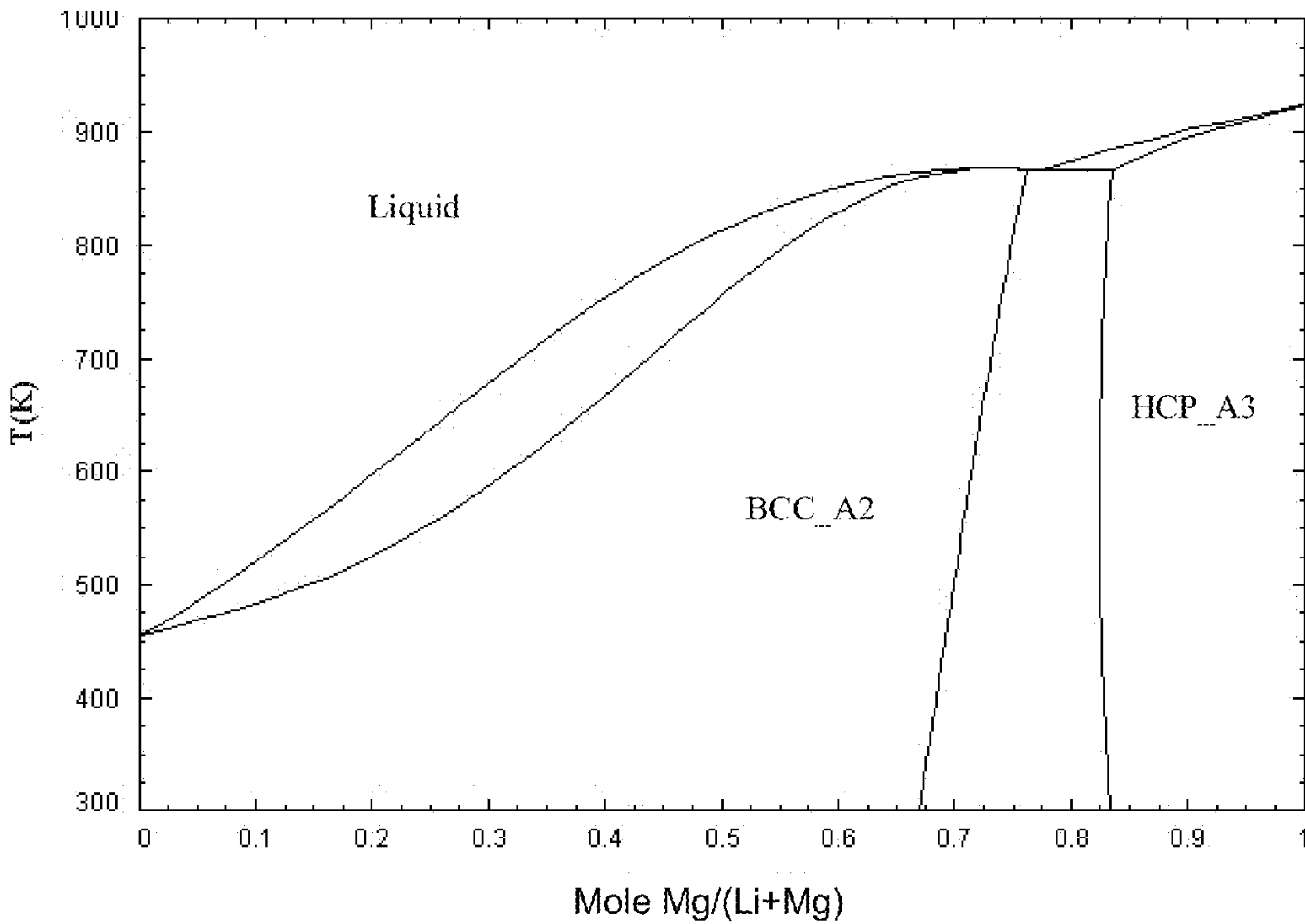


FIG. 2

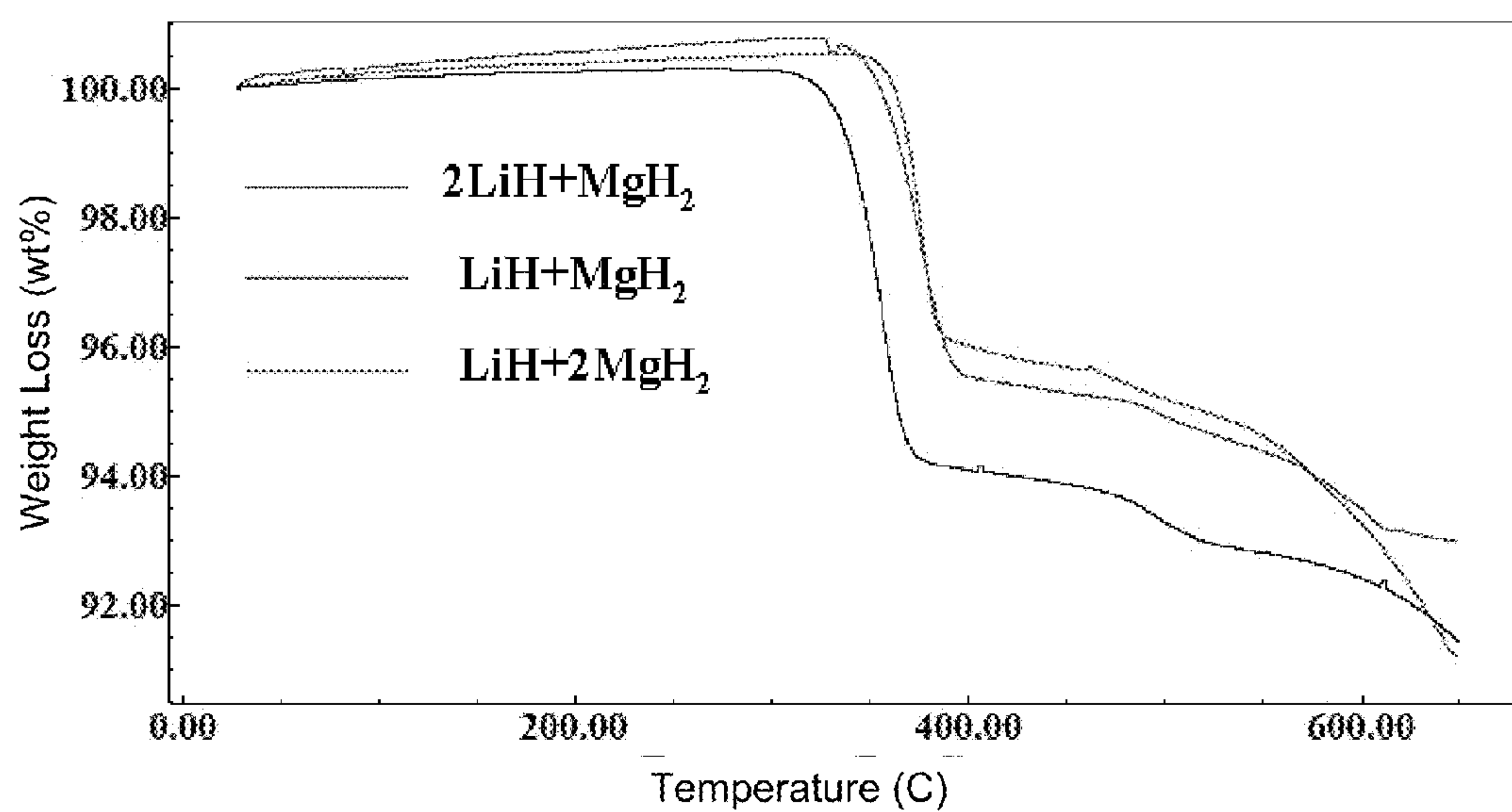


FIG. 3

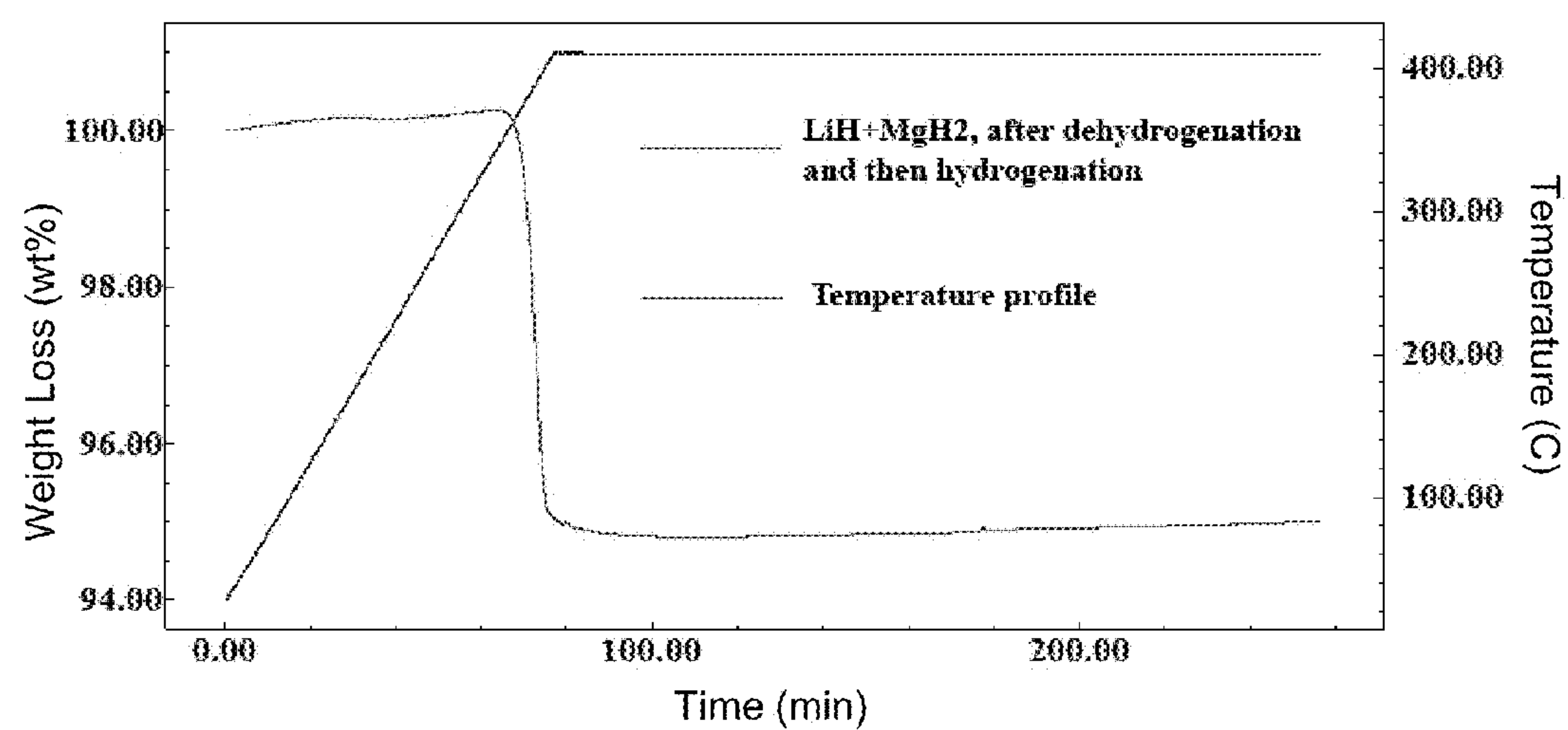


FIG. 4

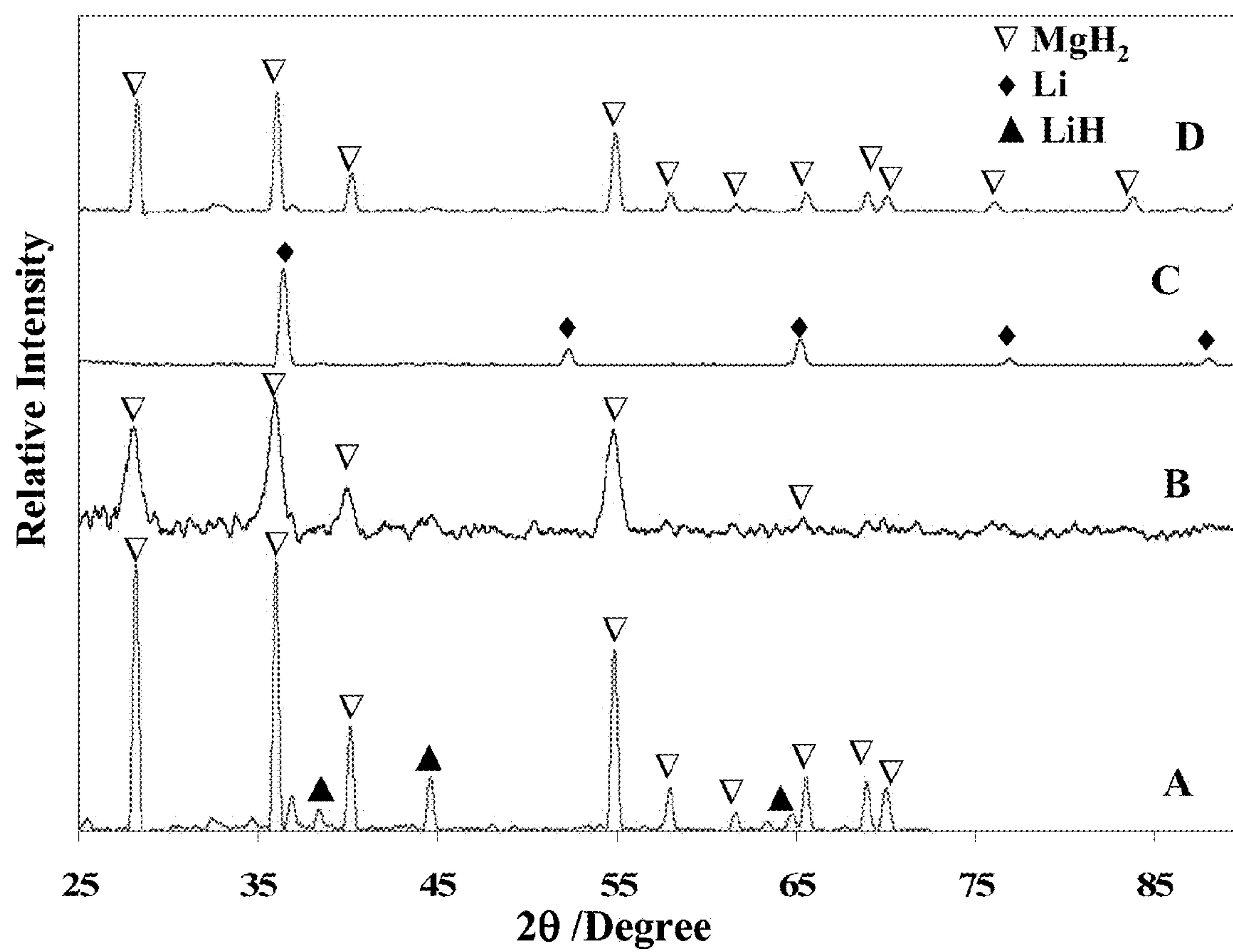


FIG. 5

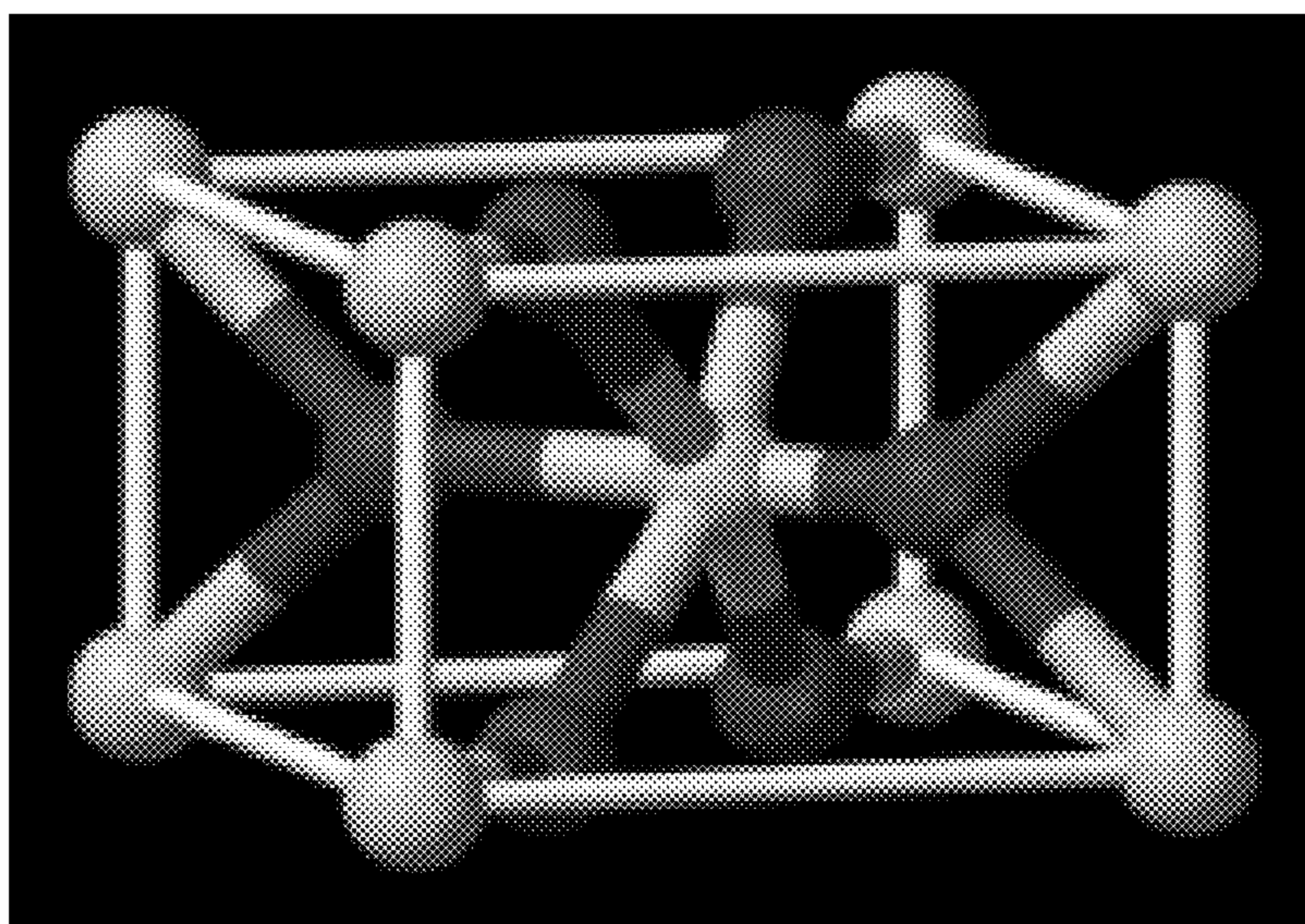


FIG. 6



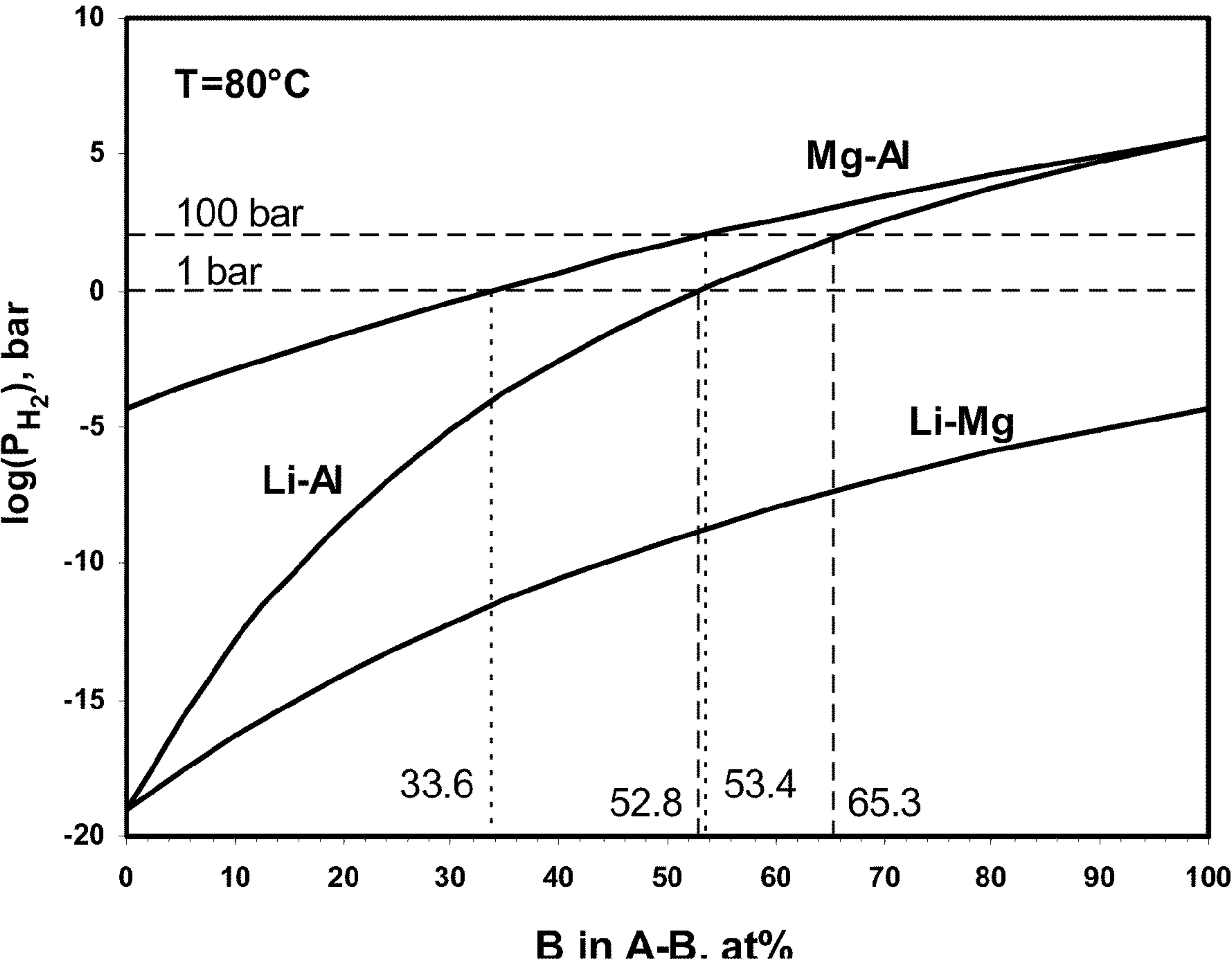


FIG. 7

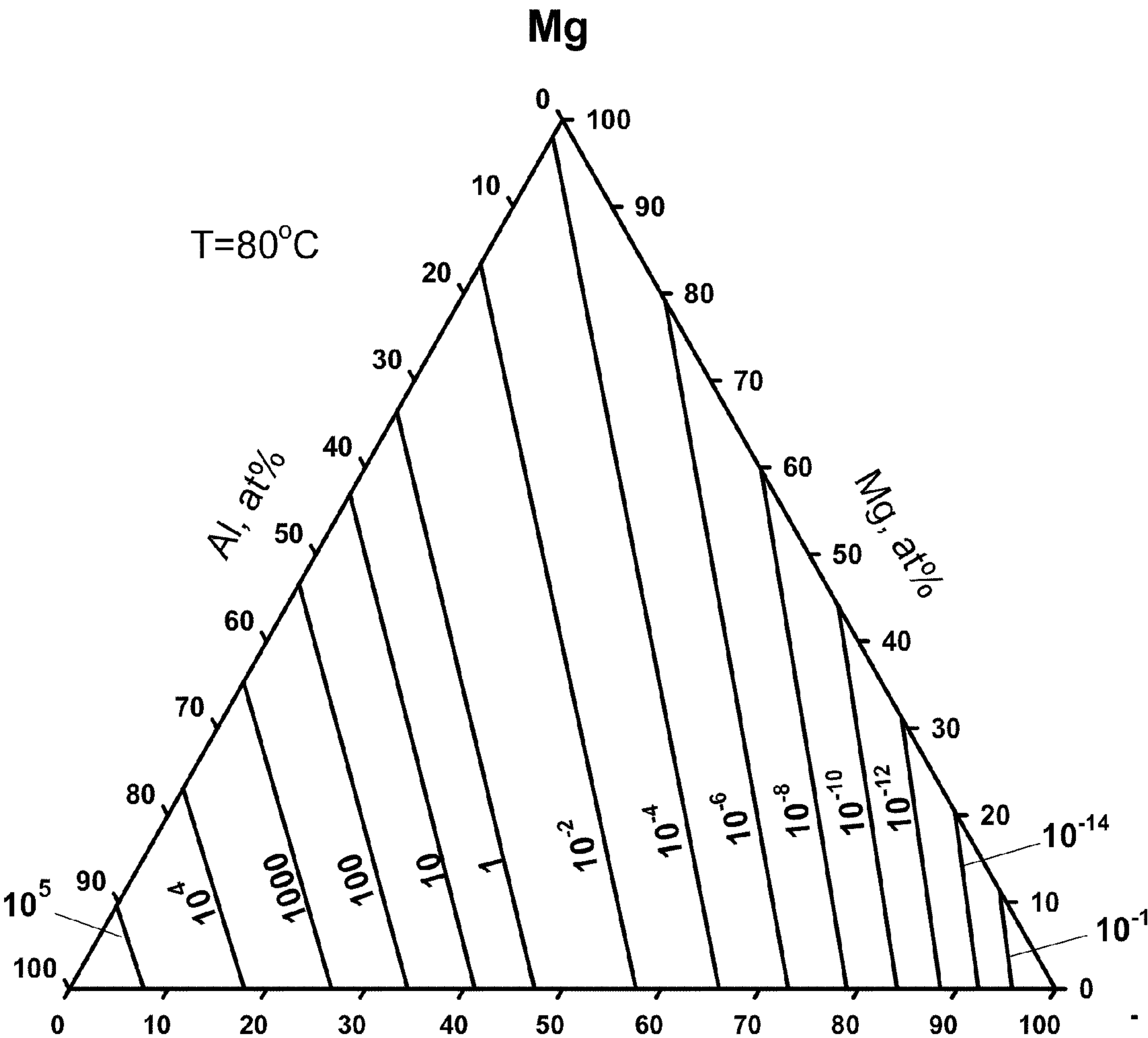


FIG. 8

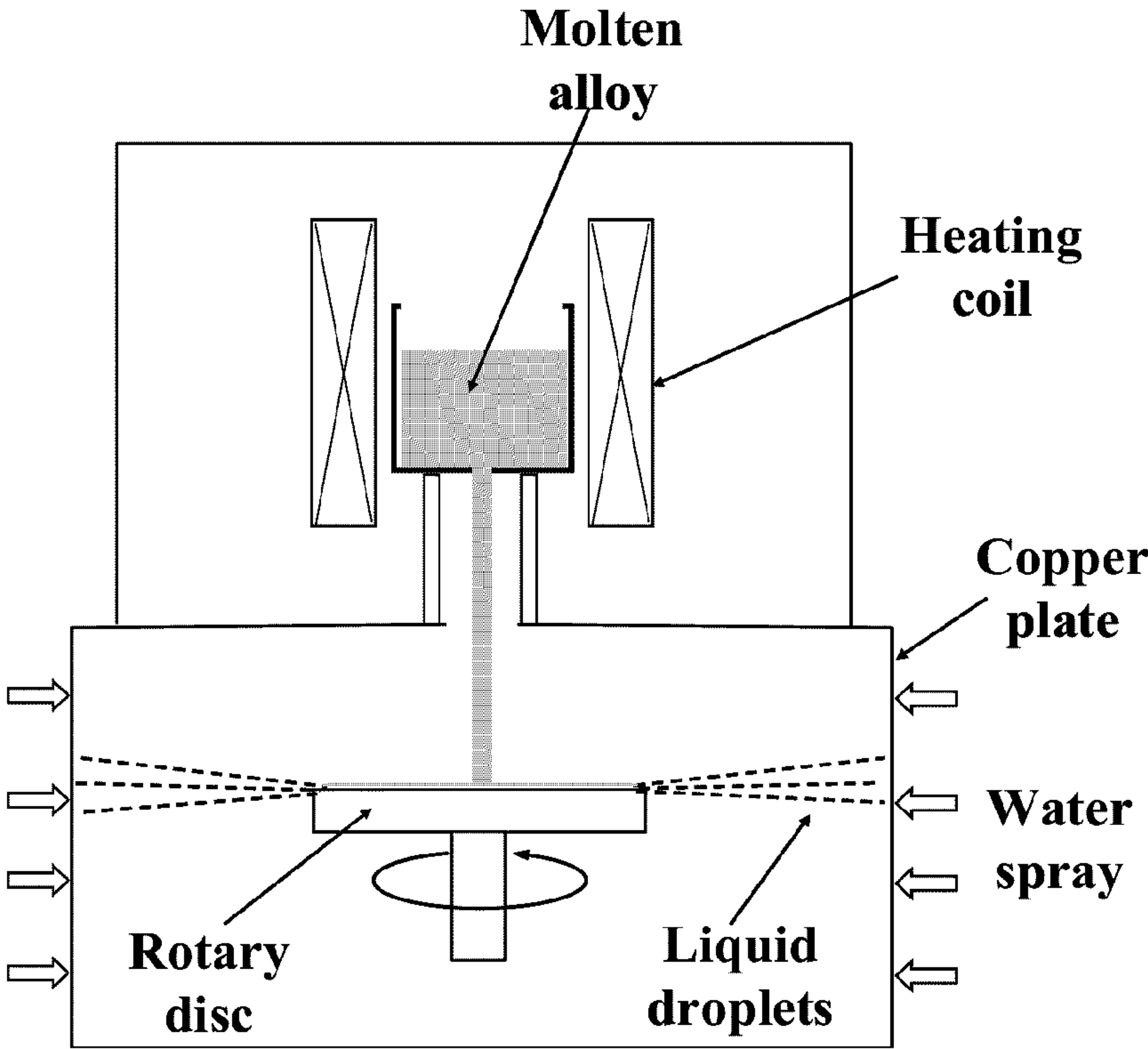


FIG. 9

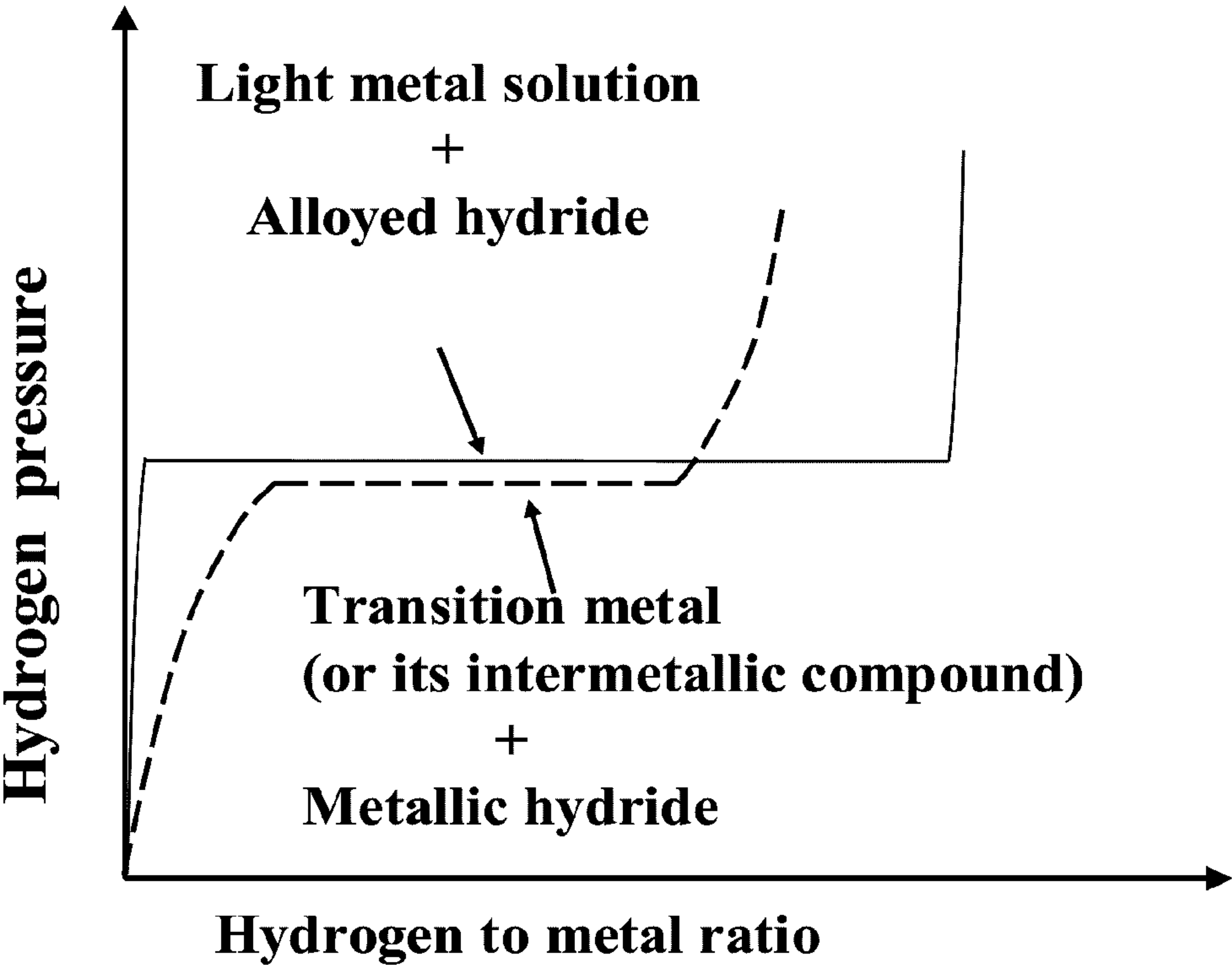


FIG. 10



## LIGHT METAL SOLID SOLUTION ALLOYS FOR HYDROGEN STORAGE

### RELATED APPLICATIONS

**[0001]** This application claims the benefit of copending U.S. Provisional Patent Application Ser. No. 61/167,990 filed on Apr. 9, 2009, which is hereby incorporated by reference in its entirety.

### GOVERNMENT INTEREST

**[0002]** This invention was made with government support under Grant No. DE-FC36-05GO15069 awarded by the Department of Energy. The United States government has certain rights in this invention.

### BACKGROUND OF THE INVENTION

**[0003]** In recent years, the search for solid hydrogen-storage materials have reemerged as a critical technology challenge that affects global environment and energy independence of this country. Although numerous materials have been studied as candidates, none known to date have demonstrated sufficient hydrogen capacity or efficiency at required operating temperature ranges.

**[0004]** Over the past decades, searches for solid hydride materials for hydrogen storage focused on intermetallic compounds that store hydrogen in interstitial spaces in the crystal lattices. More recently, focus has centered on complex metal hydrides that are inorganic salt-like compounds of anions such as  $[\text{AlH}_4]^-$ ,  $[\text{NH}_2]^-$ , and  $[\text{BH}_4]^-$ . Light metal ionic hydrides are another class of materials that have high capacity and reversibility. However, these ionic hydrides are thermodynamically too stable making dehydrogenation challenging at practical conditions.

### SUMMARY OF THE INVENTION

**[0005]** A light metal solid solution alloy (LMSSA) for reversible hydrogen storage can include a light metal solid solution alloy of  $M_1$  and  $M_2$ .  $M_1$  and  $M_2$  are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si. Furthermore, the starting materials and formation conditions are chosen such that the resulting alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.

**[0006]** A method of forming a light metal solid solution alloy for reversible hydrogen storage can comprise forming a light metal solid solution alloy of light metals  $M_1$  and  $M_2$ , wherein  $M_1$  and  $M_2$  are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si. Additionally, the alloy can have a hydrogenated state and a dehydrogenated state which are each solid solutions.

**[0007]** There has thus been outlined, rather broadly, the more important features of the invention so that the detailed description thereof that follows may be better understood, and so that the present contribution to the art may be better appreciated. Other features of the present invention will become clearer from the following detailed description of the invention, taken with the accompanying drawings and claims, or may be learned by the practice of the invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0008]** The present invention will become more fully apparent from the following description and appended

claims, taken in conjunction with the accompanying drawings. Understanding that these drawings merely depict exemplary embodiments of the present invention and they are, therefore, not to be considered limiting of its scope. It will be readily appreciated that the components of the present invention, as generally described and illustrated in the figures herein, could be arranged, sized, and designed in a wide variety of different configurations. Nonetheless, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

**[0009]** FIG. 1 is an energy diagram showing hydride destabilization of an alloy by doping (i.e. alloy formation upon dehydrogenation).

**[0010]** FIG. 2 is a Li—Mg phase diagram. Data was obtained from SETG binary alloy database.

**[0011]** FIG. 3 is a TGA curve for  $\text{MgH}_2/\text{LiH}$  at different molar ratios after high energy ball milling.

**[0012]** FIG. 4 is a TGA curve for  $\text{MgH}_2/\text{LiH}$  after dehydrogenation and rehydrogenation.

**[0013]** FIG. 5 shows XRD patterns of Mg—Li SS alloy. Line A shows  $\text{MgH}_2/\text{LiH}$  (1:1 molar ratio) after mixing, line B is  $\text{MgH}_2/\text{LiH}$  (1:1 molar ratio) after HEHP milling, line C is after dehydrogenation at  $410^\circ\text{C}$ ., and line D is after rehydrogenation at  $350^\circ\text{C}$ . and 150 bar of  $\text{H}_2$  pressure.

**[0014]** FIG. 6 is a diagram of the crystal structure of  $\beta\text{-MgH}_2$ .

**[0015]** FIG. 7 is a graph of equilibrium pressure as a function of composition for several LMSSA.

**[0016]** FIG. 8 is a ternary graph of equilibrium  $\text{H}_2$  pressure as a function of composition for Li—Mg—Al solid solutions, calculated from equation 12. Contour lines are in units of bar.

**[0017]** FIG. 9 is a schematic of a rapid solidification device.

**[0018]** FIG. 10 is a pressure-composition isotherm plot of LMSSA compared to a transition metal.

### DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

**[0019]** The following detailed description of exemplary embodiments of the invention makes reference to the accompanying drawings, which form a part hereof and in which are shown, by way of illustration, exemplary embodiments in which the invention may be practiced. While these exemplary embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, it should be understood that other embodiments may be realized and that various changes to the invention may be made without departing from the spirit and scope of the present invention. Thus, the following more detailed description of the embodiments of the present invention is not intended to limit the scope of the invention, as claimed, but is presented for purposes of illustration only and not limitation to describe the features and characteristics of the present invention, to set forth the best mode of operation of the invention, and to sufficiently enable one skilled in the art to practice the invention. Accordingly, the scope of the present invention is to be defined solely by the appended claims.

**[0020]** The following detailed description and exemplary embodiments of the invention will be best understood by



reference to the accompanying drawings, wherein the elements and features of the invention are designated by numerals throughout.

#### DEFINITIONS

**[0021]** In describing and claiming the present invention, the following terminology will be used.

**[0022]** The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a dopant” includes reference to one or more of such materials and reference to “forming” refers to one or more such steps.

**[0023]** As used herein with respect to an identified property or circumstance, “substantially” refers to a degree of deviation that is sufficiently small so as to not measurably detract from the identified property or circumstance. The exact degree of deviation allowable may in some cases depend on the specific context.

**[0024]** As used herein, “solid solution” refers to a substantially homogeneous crystalline or non-crystalline phase that includes at least two components. In particular, a solvent component forms a matrix in which a solute component is uniformly dispersed as interstitial and/or substitutional point defects.

**[0025]** As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

**[0026]** Concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a numerical range of about 1 to about 4.5 should be interpreted to include not only the explicitly recited limits of 1 to about 4.5, but also to include individual numerals such as 2, 3.5, 4, and sub-ranges such as 1 to 3, 2 to 4, etc. The same principle applies to ranges reciting only one numerical value, such as “less than about 4.5,” which should be interpreted to include all of the above-recited values and ranges. Further, such an interpretation should apply regardless of the breadth of the range or the characteristic being described. Regarding the phrase “less than,” in one embodiment, the use of such a term refers to the presence of the element in some amount; i.e., does not include zero.

**[0027]** Any steps recited in any method or process claims may be executed in any order and are not limited to the order presented in the claims. Means-plus-function or step-plus-function limitations will only be employed where for a specific claim limitation all of the following conditions are present in that limitation: a) “means for” or “step for” is expressly recited; and b) a corresponding function is expressly recited. The structure, material or acts that support the means-plus function are expressly recited in the description herein. Accordingly, the scope of the invention should be

determined solely by the appended claims and their legal equivalents, rather than by the descriptions and examples given herein.

**[0028]** Hydrogen Storage Materials

**[0029]** A new class of material, light metal solid solution alloys (LMSSA), for hydrogen storage is presented. Non-limiting examples of LMSSA can include Li—Al, Mg—Al, Li—Mg, Li—Mg—Al and Mg—Si. Among them the Li—Mg system can be a thermodynamically stable solid solution, while the others listed can be metastable which can be prepared by using non-equilibrium processes such as rapid solidification and mechanical alloying.

**[0030]** Generally, a light metal solid solution alloy (LMSSA) for reversible hydrogen storage can include a light metal solid solution alloy of  $M_1$  and  $M_2$ .  $M_1$  and  $M_2$  are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si. Furthermore, the starting materials and formation conditions are chosen such that the resulting alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.

**[0031]** Alkali and alkaline earth metals such as Li and Mg can form ionic hydrides. They can be attractive candidates for hydrogen storage because they can contain high weight percentages of hydrogen. However, the individual ionic hydrides, e.g. LiH, can be too thermodynamically stable for hydrogen storage applications, e.g. vehicular applications. The present inventors have discovered a method of destabilizing ionic hydrides without significantly sacrificing their hydrogen storage capacities. In order to destabilize LiH and  $MgH_2$ , a Li—Mg solid solution can be used in place of Li or Mg for hydrogen storage. Hydrides of Li—Mg solid solution can take advantages of the high weight capacity of these materials while being thermodynamically destabilized through alloying and optional doping. The binary phase diagram of Li—Mg shows that they form a near-isomorphous solid solution based on Li with Mg content ranging from 0 to 89 wt % at room temperature. Such a system has been discovered as unique compared to most binary A-B light metal systems, which have limited solubility of B in A.

**[0032]** Known solid solution alloys (SS-alloys) of transition metals for hydrogen storage that store hydrogen in the interstitial spaces in host metal crystal lattices tend to have low storage capacity, on the order of less than 2%. However, the present inventors have discovered light metal solid solution alloys having a reversible hydrogen weight storage capacity of greater than 5%. In one embodiment, the present alloys can have a reversible hydrogen weight storage capacity greater than about 7 wt %. Additionally, the present alloys, in contrast to an ordered compound (intermetallics), lend themselves amicably to thermodynamic tuning and engineering through alloying without changing its basic lattice structure or properties. The present disclosure provides LMSSA that form ionic hydrides that have very high hydrogen storage capacity.

**[0033]** Furthermore, in addition to Li—Mg, other LMSSA such as Li—Al, Mg—Al, Li—Mg—Al and Mg—Si can also be suitable because the thermodynamic stability of their hydrides appears to be much lower than that of the hydride of Li—Mg alloy (as discussed herein). Although these binary systems generally do not form equilibrium solid solutions that have significant solubility, they can form meta-stable solid solutions through non-equilibrium processing methods such as rapid solidification and mechanical alloying. The meta-stable structures can be retained during hydrogenation



and dehydrogenation reactions. Such alloy systems can have excellent hydrogen storage properties including capacity, reversibility, and other thermodynamic and kinetic properties.

**[0034]** Without intending to be bound by any particular theory, the LMSSA for hydrogen storage can form a “solid solution alloy of hydrides” or, perhaps, simply forms a mixture of hydrides. In any event, the term “solid solution of hydrides (SS-hydride)” will be used throughout this document to refer to a solid solution of hydride phases, not a physical mixture of discrete or single metal hydrides.

**[0035]** Regarding the particular mechanisms, Li—Mg does hydrogenate and the hydrogenated products appear to be “SS-hydrides” as XRD patterns indicated that at hydrogenated states, the “SS-hydride” has a crystal structure similar to that of  $\text{MgH}_2$  (FIG. 6). At the dehydrogenated state, the alloy had a crystal structure similar to that of Li metal. Although the exact structure and compositions of the SS-hydrides are yet to be fully characterized, the results indicated that Li—Mg can be a reversible hydrogen storage material. Additionally, in one embodiment, the Li—Mg, and other light metal solid solution alloys described herein, can have a weight capacity ranging from about 8 to about 12 wt %. The thermodynamic stability of the SS-hydrides can be drastically lower than that of LiH. The thermodynamic stability of the Li—Mg—H (hydrogenated Li—Mg) system can be tuned by alloying and/or doping the Li—Mg alloy with other elements. In one embodiment, the light metal solid solution alloys described herein can optionally contain additives such as a dopant. Non-limiting examples of suitable dopants can include B, Al, C, Si, N, Ti, Ni, Zn, Pd, Pt, Sc, Fe, Co, K, Ca, and combinations thereof.

**[0036]** Li—Mg and meta-stable solutions including Li—Al, Mg—Al, Li—Mg—Al, and Mg—Si can be similarly characterized. Synthesis of SS-alloys can be achieved using equilibrium and non-equilibrium processing methods. Hydrogenation of SS-alloys once the alloys are produced can allow determination of the structure of the SS-hydrides. In one embodiment, the light metal solid solution alloys can further include at least one additional light metal  $\text{M}_x$ , wherein x is from 3 to 6.

**[0037]** Although other combinations can be used, exemplary light metal solid solution alloys can include Li—Al, Mg—Al, Li—Mg, Li—Mg—Al, Mg—Si, and combinations thereof. Most often, the light metal solid solution alloy can be substantially free of atomic elements having an atomic mass greater than 29. As described in more detail below, the light metal solid solution alloy can also be metastable. In one embodiment, the light metal solid solution alloy can be Li—Mg. In another embodiment, the light metal solid solution alloy can be Mg—Al. In another embodiment, the light metal solid solution alloy can be Li—Al. In another embodiment, the light metal solid solution alloy can be Li—Mg—Al. In another embodiment, the light metal solid solution alloy can be Mg—Si.

**[0038]** The light metal solid solution alloys described herein can typically have a reversible hydrogen weight storage capacity from about 7 wt % to about 13 wt %, although capacities outside this range might be achieved. Depending on the particular combination, the light metal solid solution alloy can have a dehydrogenation temperature less than about 400° C. and in some cases less than about 300° C. In one embodiment, the light metal solid solution alloy can have a dehydrogenation temperature less than about 200° C. In one

embodiment, the temperature can be between 60 and 90° C. Similarly, although specific properties can vary, the light metal solid solution alloy can often have a hydrogenation pressure from about 1 bar to about 200 bar, and in one embodiment, between 1 and 100 bar.

**[0039]** Generally, a method of forming a light metal solid solution alloy for reversible hydrogen storage can comprise forming a light metal solid solution alloy of light metals  $\text{M}_1$  and  $\text{M}_2$ , wherein  $\text{M}_1$  and  $\text{M}_2$  are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si. Additionally, the alloy can have a hydrogenated state and a dehydrogenated state which are each solid solutions.

**[0040]** The light metal solid solution alloy can be formed using any number of approaches as long as the solid solution characteristics are maintained. Light metals  $\text{M}_1$  and  $\text{M}_2$  can be provided as elemental sources or compounds. Elemental sources can be suitable but generally involve extra care to avoid exposure to oxygen. Each of  $\text{M}_1$  and  $\text{M}_2$  are different and independently selected from Li, Mg, Al, Na, Be, and Si. The selection of starting materials and formation process can be chosen such that the final alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.

**[0041]** In one aspect, each of  $\text{M}_1$  and  $\text{M}_2$  can be provided as elemental metals. In another aspect, each of  $\text{M}_1$  and  $\text{M}_2$  can each be provided as metal hydrides. Alternatively, one can be provided as an elemental metal while the other can be provided as a hydride.

**[0042]** Although other methods can be suitable, two methods are of particular interest. Mechanical alloying of the starting materials can reduce particle size and create sufficient mixing to form a solid solution. High energy ball milling is one example. One specific embodiment involves mechanical alloying using a high energy high pressure planetary milling machine. In another alternative, rapid solidification can be used to form the solid solution. Centrifugal atomization is one particular example of a highly suitable rapid solidification process and can be used in one embodiment.

**[0043]** In some embodiments it can be desirable to include additional components to the solid solution. Such additives can be designed to provide a variety of benefits such as, but not limited to, destabilization of hydrides, structural integrity, filler, etc. In one specific aspect, a doping element can be included with the light metals.

**[0044]** Although other physical forms can be suitable, typically the solid solution can be a nanoparticulate material. As a general guideline, the grain size can be from about 5 nm to about 100 nm, and in some cases to about 15 nm.

## EXAMPLES

**[0045]** The following examples illustrate a number of embodiments of the present compositions, systems, and methods that are presently known. However, it is to be understood that the following are only exemplary or illustrative of the application of the principles of the present compositions, systems, and methods. Numerous modifications and alternative compositions, methods, and systems may be devised by those skilled in the art without departing from the spirit and scope of the present systems and methods. The appended claims are intended to cover such modifications and arrangements. Thus, while the present compositions, systems, and methods have been described above with particularity, the following examples provide further detail in connection with what are presently deemed to be the acceptable embodiments.



**[0046]** General Background

**[0047]** The present inventors have discovered light metal solid solution alloys that are reversible, have good thermodynamics and kinetics, and can have excellent hydrogen storage capacity as opposed to previously known metal hydrides that may meet general temperature and kinetics requirements, but are far short of meeting the hydrogen capacity target. Complex hydrides meet the capacity requirements, but are far short of reaching the temperature and kinetics targets.

**[0048]** Solid hydrides can be broadly classified into four categories: 1) Ionic hydrides, 2) Covalent hydride, 3) Metal hydrides, and 4) Complex hydrides. The following review illustrates the basic differences of these hydrides.

**[0049]** Ionic Hydrides

**[0050]** In ionic hydrides with a typical formula of  $M_xH_y$ , hydrogen exists as  $H^-$  and M is mainly alkali or alkaline earth metals. Almost all simple ionic hydrides such as LiH, do not have protonic transport that works for the transition metal hydrides. (In transition metal hydrides, the metal atom effectively changes valence as the hydrogen is added.) For ionic hydrides, the addition of hydrogen must involve the complete geometric rearrangement of the lattice. Ionic hydrides are therefore too thermodynamically stable.

**[0051]** Covalent Hydrides

**[0052]** In covalent hydrides, hydrogen shares the electron pair with non-metal atoms with similar electronegativities. Examples of covalent hydride include  $H_2O$ ,  $H_2S$ ,  $SiH_4$ , hydrocarbons, and so forth.

**[0053]** Metal Hydrides

**[0054]** Metal hydrides, as generally defined in the art, are formed by transition metals including the rare earth and actinide series with hydrogen. Because the thermodynamic stabilities of metal hydrides that contains only one metal are too high, most metal hydrides of interest are alloys or intermetallics of two or more metals. The intermetallics can be generalized as  $A_xB_y$ , where A is an early transition metal, rare-earth metal, or Mg. Metal B (e.g. Ni, Co, Cr, Fe, Mn, or Al) typically does not form stable hydrides. Examples include  $LaNi_5H_{6.5}$ ,  $TiFeH_2$ , and  $Mg_2NiH_4$ . A common feature of the metal hydrides is that they are non-stoichiometric interstitial compounds with hydrogen occupying either tetrahedral or octahedral interstices. During hydrogenation process, the metal phase transforms from  $\alpha$  to  $\beta$ . An  $\alpha$  phase is a solid solution of H in the host metal, while  $\beta$  is the hydride phase with metallic bonds between hydrogen and the host metal.

**[0055]** For most metal hydrides as known in the art, there is little solubility of B in A in binary A-B systems. For example,  $Mg_2Ni$  is a well studied intermetallic alloy for  $H_2$  storage. Mg has no solubility for Ni at moderate temperatures. In some cases, A and B are completely immiscible. For example, no thermodynamically stable alloys can be formed between Mg and Ti, or Mg and Co at any composition. However, as mentioned earlier, there has been some effort on using solid solution of transition metals including that of Pd-, V-, Ti, Nb, and Zr-based SS-alloys.

**[0056]** Regarding the properties of metal hydrides, intermetallic hydrides such as  $LaNi_5$  ( $AB_5$ ), generally speaking, work well within the desired temperatures. However, the storage capacities of intermetallic metal hydrides are generally less than 2 wt %, which is too low to meet the requirement of fuel cell vehicle applications.

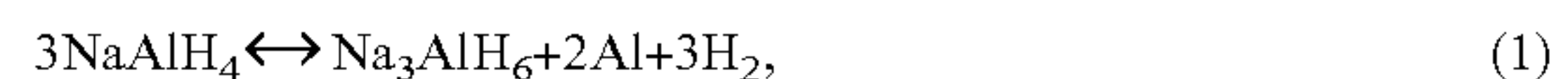
**[0057]** Magnesium hydride ( $MgH_2$ ) is one exception that it contains a relatively high percentage of hydrogen (theoretically 7.7 wt %). However, the equilibrium hydrogen pressure

of  $MgH_2$  at 60-90° C. is too low, or the temperature required for  $MgH_2$  to reach 1 bar pressure of hydrogen is too high (~275° C.). The intermetallic alloy of  $Mg_2NiH_4$  has better thermodynamic properties than pure  $MgH_2$ , but, the gravimetric capacity of  $Mg_2NiH_4$  is severely penalized down to 3.58 wt %.

**[0058]** Aluminum hydride,  $AlH_3$ , is another exception. It is a very unstable hydride near room temperatures.  $AlH_3$  is very easy to dehydrogenate; however, it is very difficult to rehydrogenate because of its extremely high equilibrium pressure (~7 GPa at room temperature).

**[0059]** Complex Hydrides—Salts of Alkaline Metal of  $(AlH_4)^-$ ,  $(NH_2)^-$ , and  $(BH_4)^-$

**[0060]** The term “complex hydride”, as generally used in the art, refers to inorganic salt-like compounds of anions such as  $[BH_4]^-$ ,  $[AlH_4]^-$ , and  $[NH_2]^-$ , stabilized with light metal cations. Examples of complex hydrides include  $NaAlH_4$ ,  $LiBH_4$ , and  $LiNH_2$ . Sodium aluminum hydride,  $NaAlH_4$ , with titanium additives can reversibly store up to 5 wt % of hydrogen by the following reaction steps:



**[0061]** Prior to the present disclosure, the reverse reactions (eqn. 1 and 2) were known to be very difficult. However, the capacity of  $NaAlH_4$  is still rather low, i.e., on the order of 3 to 5 wt %, and the above reactions still suffer from issues related to kinetics.

**[0062]** As such, the above discussion illustrates some of the differences between known materials in the art and the compositions of the present disclosure.

## Example 1

## Thermodynamic Tuning, Destabilization, and Methods to Improve Kinetics

**[0063]** To help improve thermodynamic and kinetic properties of solid hydrogen storage materials, a number of methods can be employed.

**[0064]** Nano-engineering: To overcome the kinetic barriers, nano-engineering approaches can include: a) Mechanical ball milling to produce nanosized particles; b) Nanoscaled thin film studies; and c) Nano-porous materials such as carbon aerogels that function as a scaffold with nanosized pores. Nanosize scale can affect not only the kinetics of reactions, but also the thermodynamics. However, the use of nano porous materials as scaffold can suffer from penalty in loss of capacity.

**[0065]** Catalysis: Using catalysts can be a straight forward method to improve kinetics of chemical reactions. The effects of titanium, nano-Ni, and Pd have shown some positive activity. Unfortunately, to date, the positive effects of catalysts are not sufficient with regard to transforming all materials, e.g.  $LiBH_4$ , from unsatisfactory to satisfactory.

**[0066]** Thermodynamic tuning and destabilization: The concept of destabilization of complex hydrides is a broad concept that can be said of many materials and methods that are applied to improve the performance of solid hydrides for hydrogen storage. For example, in an attempt to destabilize  $MgH_2$ , Si can be added to react with  $MgH_2$  according to equation 3. It was rationalized that by adding Si, the thermodynamics of the dehydrogenation of  $MgH_2$  can be tuned as



shown by FIG. 1, where side (a) illustrates a generic A element and side (b) illustrates the Mg system.



**[0067]** From a perspective of liberating  $\text{H}^-$  that was bond to  $\text{Mg}^{2+}$ , the reaction (eqn. 3) is completely successful, which is attributed to the fact that the free energies including the change of enthalpies of equation 3 is more favorable than that of the direct decomposition reaction of  $\text{MgH}_2$  to Mg and  $\text{H}_2$  (eqn. 4). Unfortunately, the reverse reaction of equation (3) has not been demonstrated.



**[0068]** From a more narrow perspective, reaction 3 is not a direct change of the thermodynamics of reaction (4); rather, it is a complete new reaction.

**[0069]** In contrast to this approach of using a new reaction to achieve destabilization effect, the methods described in the present disclosure can provide a meta-stable Mg—Si SS-alloy without ever forming  $\text{Mg}_2\text{Si}$ . Hydrogenation of an Mg—Si meta-stable solid solution can be kinetically as well as thermodynamically feasible.

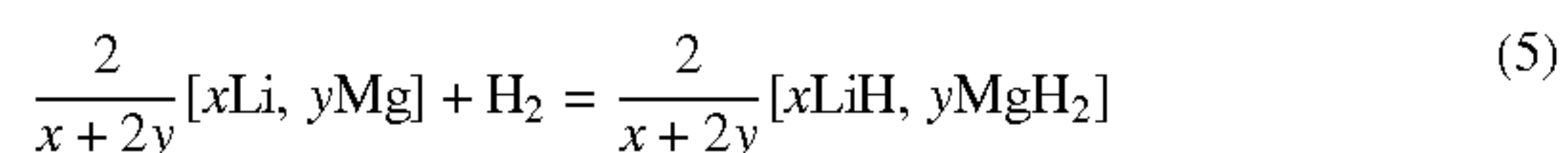
**[0070]** While the embodiments of the present disclosure do not necessarily rely upon the above methods in achieving the highly efficient reversible hydrogen storage materials described herein, these methods can be used in conjunction with the present methods.

## Example 2

### Light Metal Solid Solution Alloys for Hydrogen Storage

**[0071]** Overview

**[0072]** Given the disadvantages of metal hydrides (low capacity) and complex hydrides (thermodynamic stability and poor kinetics) and the need to develop materials that have better prospects from both capacity and thermodynamic perspectives, a new class of material systems based on light metal solid solution alloys (LMSSA) for hydrogen storage has been discovered. In some cases, the solid solution alloys (SS-alloys) are meta-stable solutions. Using Li—Mg as a model, a reversible hydrogenation and dehydrogenation can be described as follows:



**[0073]** Based on general thermodynamic principles of solutions, it can be stated that the thermodynamics of solid solution systems such as those mentioned above, in either hydrogenated or dehydrogenated state, can be engineered by using alloying or doping elements that change the activities of the reaction components within the solutions.

**[0074]** Li—Mg can form a near-isomorphous solid solution with 0 to 85 wt % of Mg at moderate temperatures (see FIG. 2). A Li—Mg solid solution which is hydrogenated and forms a solid solution of hydrides, or SS-hydride, denoted either as  $[\text{xLiH}, \text{yMgH}_2]$  or simply as  $(\text{Li}, \text{Mg})\text{H}_x$ , that is not a physical mixture of LiH and  $\text{MgH}_2$  ( $\text{xLiH} + \text{yMgH}_2$ ), the hydrogenated product  $(\text{Li}, \text{Mg})\text{H}_x$  can be thermodynamically less stable than  $(\text{xLiH} + \text{yMgH}_2)$ .

**[0075]** The hydride of Li—Mg alloy has a theoretical hydrogen storage weight capacity higher than that of  $\text{MgH}_2$

and lower than LiH, i.e. from 7.7 to 12.5 wt %, dramatically higher than that of any interstitial metal hydrides. Kinetically, the SS-hydride of Li—Mg can be engineered to be as satisfactory as that of  $\text{MgH}_2$ , which has been shown to be excellent when  $\text{MgH}_2$  is made into nanosized particles with catalytic additives. The thermodynamic properties of the SS-hydrides of Li—Mg alloy can be tunable by adding other alloying elements and varying relative Li and Mg contents.

**[0076]** The concept on using Li—Mg solid solution can be extended to other binary light metal alloys such as Li—Al, Mg—Al, Li—Mg—Al, and Mg—Si. However, these alloys generally do not form solid solutions with significant solubility. Therefore, meta-stable solid solutions can be considered in these cases. For example, using Li—Al, hydrogenated products of a Li—Al alloy should have a thermodynamic stability between that of LiH and  $\text{AlH}_3$ , which could be ideal for practical applications. One consideration for Li—Al system can be that the Li—Al meta-stable solid solution be stable enough without decomposing into two phase mixtures of Li or Al and their intermetallics phases such as LiAl,  $\text{Li}_2\text{Al}_3$ ,  $\text{Li}_4\text{Al}_9$ , or  $\text{LiAl}_3$ .

**[0077]** To briefly summarize, the LMSSA for hydrogen storage is a new and distinctively different approach than those used in the prior art. Compared to complex hydrides, the proposed system can have better reversibility, kinetics, lower thermodynamic stability, and less complexity during dehydrogenation and hydrogenation. In addition, using the proposed LMSSA, there will be no possibility of forming any undesired gases during dehydrogenation.

**[0078]** Experimental Results

**[0079]** Based on the concept described above, a preliminary investigation was carried out using Li—Mg as a model material. A few key findings are presented below to illustrate the concept.

**[0080]** First, experiments were carried out to demonstrate reversible “dehydrogenation  $\leftrightarrow$  hydrogenation” reactions. Commercial LiH and  $\text{MgH}_2$  powders were mixed at 1:2, 1:1, and 2:1 molar ratios, respectively, and mechanically high energy ball milled to nanosized particles. The as-milled powders were analyzed using TGA to measure dehydrogenation weight loss versus temperature. Assuming all weight loss was due to  $\text{H}_2$  release, FIG. 3 shows that the mechanically alloyed hydrides release hydrogen at two stages.

**[0081]** The first stage of the 1:1 mixture starts at  $\sim 320^\circ\text{C}$ . producing approximately 6.3 wt %  $\text{H}_2$ . This amount of hydrogen is significantly higher than what would be possible just from the  $\text{MgH}_2$  contained in the mixture (theoretical 5.83 wt %), indicating that there may be a new SS-hydride that produces hydrogen at a relatively low temperature (relative to LiH) with an impressive rapid rate. The dehydrogenation temperature of the second stage is also lower than that of pure LiH, which is an encouraging indication of the destabilization of LiH.

**[0082]** The dehydrogenated mixture was then hydrogenated at  $350^\circ\text{C}$ . under 150 bar pressure (e.g. the pressure is higher than what is needed, but is used to ensure results in this example). The hydrogenated product is then also analyzed using TGA, as shown in FIG. 4. TGA curve for the hydrogenated sample showed almost the same dehydrogenation behavior as that of the as-milled powder ( $\text{MgH}_2 + \text{LiH}$ , green curve in FIG. 3), indicating that the SS-hydride prior to dehydrogenation is re-formed in the hydrogenation experiment.

**[0083]** The powders at various stages of the experimental cycle, including the as-mixed (without milling) powder, as-

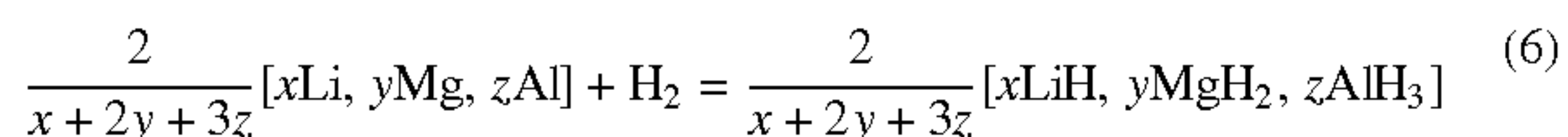


milled powder, powder after first dehydrogenation cycle, powder after re-hydrogenation, and powder after the second dehydrogenation, were all analyzed using XRD. The results are given in FIG. 5, using the powder with 1:1 molar ratio of LiH:MgH<sub>2</sub> as an example. Compared to the as-mixed sample, the as-milled one has no strong signal from LiH, which suggests that either LiH was completely amorphous after milling, or the LiH and MgH<sub>2</sub> mixture was mechanically alloyed forming a new SS-hydride phase with a crystal structure similar to that of MgH<sub>2</sub>, as shown in FIG. 6. After dehydrogenation at 410° C., the only dominate XRD pattern is that of Li metal, or most likely a Li—Mg solid solution alloy (FIG. 5C). This shows that the hydrogen in LiH was at least partially liberated, or one would expect Mg metal to be present in the XRD pattern. After rehydrogenation, MgH<sub>2</sub>-type phase was reformed as shown in FIG. 5D. The exact atomic structure and stoichiometry of the hydrogenated solution, i.e. SS-hydride of Li—Mg alloy are unclear.

**[0084]** In short, the results indicate that the SS-alloy of Li—Mg can be hydrogenated and form an SS-hydride of Li—Mg alloy. The reaction is reversible. The reaction kinetics seems to be sufficiently fast at the selected temperatures. The temperature required for rapid reactions is dramatically reduced compared to that of LiH.

**[0085]** Thermodynamic Feasibility Analysis

**[0086]** Based on the reversible hydrogen storage reaction between a solid-solution of metals and a solid-solution of hydrides, the dependence of equilibrium H<sub>2</sub> pressure as a function of compositions and temperature can be established by thermodynamic analysis. Here, Li—Mg—Al is used as a model system in the following analysis although similar analysis can be applied to other LSSA systems. It should be noted that because LiH and MgH<sub>2</sub> is very stable up to high temperatures and AlH<sub>3</sub> is unstable even at room temperature, a solid solution of LiH, MgH<sub>2</sub> and AlH<sub>3</sub> is intuitively very interesting. The hydrogenation reaction of Li—Mg—Al is



$$\Delta G^\circ = \frac{2}{x+2y+3z} (x\Delta G_{\text{LiH}}^\circ + y\Delta G_{\text{MgH}_2}^\circ + z\Delta G_{\text{AlH}_3}^\circ) = \quad (7)$$

$$RT \ln P_{\text{H}_2} + RT \ln \left( \frac{x_{\text{Li}}^x \cdot x_{\text{Mg}}^y \cdot x_{\text{Al}}^z}{x_{\text{LiH}}^x \cdot x_{\text{MgH}_2}^y \cdot x_{\text{AlH}_3}^z} \right) + RT \ln \left( \frac{r_{\text{Li}}^x \cdot r_{\text{Mg}}^y \cdot r_{\text{Al}}^z}{r_{\text{LiH}}^x \cdot r_{\text{MgH}_2}^y \cdot r_{\text{AlH}_3}^z} \right)$$

**[0087]** where  $\Delta G^\circ$  is the standard Gibbs free energy of reaction 6;  $\Delta G_{\text{LiH}}^\circ$ ,  $\Delta G_{\text{MgH}_2}^\circ$  and  $\Delta G_{\text{AlH}_3}^\circ$  are standard Gibbs formation energies of LiH, MgH<sub>2</sub> and AlH<sub>3</sub> [70];  $P_{\text{H}_2}$  is the equilibrium H<sub>2</sub> pressure, bar;  $x_{\text{Li}}$ ,  $x_{\text{Mg}}$  &  $x_{\text{Al}}$  and  $r_{\text{Li}}$ ,  $r_{\text{Mg}}$  &  $r_{\text{Al}}$  are molar fractions and activity coefficients of Li, Mg and Al in SS-alloy [Li—Mg—Al] or [xLi, yMg, zAl];  $x_{\text{LiH}}$ ,  $x_{\text{MgH}_2}$  &  $x_{\text{AlH}_3}$  and  $r_{\text{LiH}}$ ,  $r_{\text{MgH}_2}$  &  $r_{\text{AlH}_3}$  are molar fractions and activity coefficients of LiH, MgH<sub>2</sub> and AlH<sub>3</sub> in SS-hydride (Li,Mg,Al)H<sub>x</sub> or [xLiH, yMgH<sub>2</sub>, zAlH<sub>3</sub>].

**[0088]** Since the molar fractions of Li, Mg and Al in SS-alloy are equal to the molar fractions of LiH, MgH<sub>2</sub> and AlH<sub>3</sub> in their SS-hydrides, the second term in the right-side of equation 7 is zero. Moreover, the third term is assumed to be zero as well, since the data of activity coefficients of this system are not available.

**[0089]** Thus, the dependence of the equilibrium H<sub>2</sub> pressure as a function of temperature and composition of Li—Mg—Al system is obtained as follows

$$P_{\text{H}_2} = \exp \left( \frac{2}{x+2y+3z} \frac{(x\Delta G_{\text{LiH}}^\circ + y\Delta G_{\text{MgH}_2}^\circ + z\Delta G_{\text{AlH}_3}^\circ)}{RT} \right) \quad (8)$$

**[0090]** For other binary, ternary or multi-component solid solution systems, the dependence of the system's equilibrium H<sub>2</sub> pressure can be established in similar analysis.

**[0091]** The calculated results for the three binary systems, Li—Al, Mg—Al and Li—Mg at T=80° C. are plotted in FIG. 7. It is clear that the equilibrium H<sub>2</sub> pressure of any binary alloy is located between that of two constituent metals and changes monotonically with the alloy composition. For Li—Al and Mg—Al,  $P_{\text{H}_2}$  increases dramatically with Al content; while for Li—Mg,  $P_{\text{H}_2}$  increases dramatically with Mg content. Suppose that the operational range of  $P_{\text{H}_2}$  is 1 to 100 bar, then the suitable alloy composition range can be determined from FIG. 6 to be 52.8-65.3 at % Al for Li—Al and 33.6-53.4 at % Al for Mg—Al. These equilibrium pressures can be ideal for hydrogen storage.

**[0092]** However, if Al is added to Li—Mg solid solutions to form Li—Mg—Al ternary solid solutions, suitable equilibrium H<sub>2</sub> pressure can be obtained in a wide range of alloy compositions, as shown by the area enclosed by the two contour lines of  $P_{\text{H}_2}=1$  bar and  $P_{\text{H}_2}=100$  bar in the contour plot of  $P_{\text{H}_2}$  in the ternary system at 80° C. (FIG. 8).

**[0093]** With regard to Li—Al system, it should be noted that, using conventional chemical methods, Li and Al reactions with hydrogen to form lithium alanates—LiAlH<sub>4</sub> or Li<sub>3</sub>AlH<sub>6</sub>, which are also attractive candidates for H<sub>2</sub> storage. Unfortunately, these ordered compounds of lithium alanates have poor reversibility once decomposed into LiH and Al. In contrast, according to the thermodynamic analysis given above, hydrogenation of a Li—Al metal solution prepared by non-equilibrium processes can be much more thermodynamically favorable than that of LiH+Al. The hydrogenated solution (Li,Al)H<sub>x</sub> can also have significantly different properties from that of LiAlH<sub>4</sub>.

**[0094]** As a summary, the equilibrium H<sub>2</sub> pressure of a SS-alloy is located in between the equilibrium H<sub>2</sub> pressures of the single metal hydrides of the constituent elements. To achieve a desired  $P_{\text{H}_2}$ , a SS-alloy consisting of elements with higher than the desired  $P_{\text{H}_2}$  (e.g., Al) and elements with lower than desired  $P_{\text{H}_2}$  (e.g., Li, Mg) can be designed.

**[0095]** Kinetic Feasibility and Stability of Meta-Stable Solid Solutions

**[0096]** Using Li—Mg as an example, Mg is a substitutional solute in the Li matrix with BCC structure. When the alloy is hydrogenated, it forms an SS-hydride with a structure similar to that of MgH<sub>2</sub>, i.e. the rutile structure as shown in the following FIG. 6. The structural transformation from BCC to tetragonal structures would have kinetic barriers to overcome. At present time, predictions of the kinetics of these reactions are difficult. In general, because metastable solid solutions have moderate equilibrium hydrogen pressures (as shown in the thermodynamic feasibility section) and the microstructure of non-equilibrium solid solutions would be less dense than that of equilibrium alloys, it is expected that these metastable solid solutions would have lower kinetic barrier than their single-element hydride counterparts.

**[0097]** The second issue with regard to meta-stable SS-alloys is the stability of the solid solutions. The reversible hydrogen storage reaction between a solid-solution of metals



and a solid-solution of hydrides is essentially based on the assumption that both the solid-solution of relevant metals and the solid-solution of relevant metal hydrides can be formed and is stable during hydrogenation and dehydrogenation process.

**[0098]** The existence of meta-stable solid solution has been well documented by the production of extensive range of rapid solidified alloys, including Al-based alloys, while the synthesis of SS-hydride of Li—Mg alloy as described in the previous section gave an indication of the existence of meta-stable solid solutions of hydrides. Identifying a general trend, the phase transformations of metallic glass made by rapid solidification techniques are discussed. There are three characteristic temperatures during transformation of a metallic glass: crystallization temperature  $T_x$ , critical temperature  $T_c$ , and melting temperature  $T_m$ .  $T_c$  is always lower than  $T_x$ . At  $T_x > T > T_c$ , the crystallization of metal glass will yield two- or multi-phase structures through nucleation and growth mechanisms; while at  $T < T_c$ , the final structure after crystallization is usually a single phase of meta-stable solid solution. In other words, below  $T_c$  the meta-stable solution will be kinetically stable.  $T_x$  can be correlated with the melting point  $T_m$  of the material as  $T_x = (0.4 \sim 0.65)T_m$  in K; while  $T_c$  is usually around 100K lower than  $T_x$ . For Li—Al with a composition (52.8-65.3 at % Al),  $T_m$  is found to be approximately 950K based on the Li—Al phase diagram.  $T_c$  can thus be estimated as  $(0.4 \sim 0.65) \times 950 - 100 = 280 \sim 517.5$ K. Therefore, at the desired hydrogenation and dehydrogenation temperature of 60-90° C., Li—Al meta-stable solid solution can be kinetically stable. Similar inference can be drawn for Mg—Al and Li—Mg—Al. A higher stability of Mg—Si solution can be expected due to its higher melting temperature. In addition, other alloying elements can be used to stabilize the meta-stable solutions.

#### Example 3

##### Synthesis of Li—Mg Alloy and their Hydrides

**[0099]** Although Li—Mg does not have the most potential for  $H_2$  storage at low temperatures according to the thermodynamic feasibility analysis, it is an excellent material as a model system. Two exemplary methods in combination to prepare selected Li—Mg alloys include a high pressure autoclave and a unique high energy high pressure mechanical milling technology.

**[0100]** To use the autoclave, large pieces of Li and Mg can be mixed and placed in a stainless steel crucible, and heated in the autoclave to appropriate temperatures (400 to 700° C.) in a high purity argon atmosphere. The custom-made autoclave has 5000 psi hydrogen pressure capacity and a programmable temperature control unit. Li will melt at 181° C., dissolve Mg, and form Li—Mg solid solution.

**[0101]** Because the extreme sensitivity of Li metal to air, an alternative is to use LiH and  $MgH_2$  as starting raw materials. The LiH/ $MgH_2$  mixture can be first mechanically alloyed using a unique high energy high pressure (HEHP) milling machine. The as-milled powder can be placed in the autoclave and heated to 600° C. until all hydrogen is released. The product of such a complete dehydrogenation can be Li—Mg solid solution.

**[0102]** The Li—Mg SS-alloy can be hydrogenated in the autoclave. The autoclave can be connected to a panel of valve systems that allow switching between vacuum and atmospheres including Ar, He,  $N_2$ , or  $H_2$  without ever exposing the sample to air.

**[0103]** The autoclave can also be equipped with a sample transfer device. Powders can be sealed off in the device and then transferred into a glove box with an antechamber. The glove box has constantly circulated Ar with less than 1 ppm oxygen.

#### Example 4

##### Synthesis of Meta-Stable Solid Solutions and their Hydrides

**[0104]** As mentioned earlier, Li—Al, Mg—Al, Li—Mg—Al and Mg—Si do not form solid solutions with appreciable solubility. In order to prepare their meta-stable SS-alloys, non-equilibrium processing techniques can be used. For example two techniques: rapid solidification and high energy high pressure mechanical alloying can be used.

**[0105]** FIG. 9 illustrates a rapid solidification process (Centrifugal Atomization) which can be used. The alloy can be melted in a crucible (stainless steel, graphite, or ceramic depending on the alloy's reactivity). The melt can be streamed onto the high-speed-rotating disc, on the periphery of which the liquid is thrown off in the form of very fine droplets. As soon as the liquid droplets reach the surrounding water-spray-cooled copper plate, they can be rapidly quenched at a cooling rate of  $10^5$ - $10^7$  K per second into powders of meta-stable solid solutions. The entire set up can be under vacuum or inert atmosphere to avoid oxidation or other contaminations. A transfer device can also be equipped on the RS set up to transfer powders into an argon protected glove box.

**[0106]** Non-equilibrium SS-alloys and/or SS-hydride can also be prepared using the aforementioned HEHP process. The HEHP machine can be a unique planetary milling machine. Compared to commercial planetary machines, the HEHP unit has a very large gyration arm radius. The maximum acceleration is 100 g force. The critical milling speed can be controlled and adjusted based on specific charge material and milling media. Such a technique has been used to prepare other nanosized metal hydride powders. For example, the  $MgH_2$ — $TiH_2$  material processed using the HEHP process had a grain size from 5 to 15 nanometers. It should be noted, however, that the high energy mechanical alloying method may be more effective for preparing alloys of hydrides rather than light metals, because most of the light metals are extremely ductile and difficult to fracture, while their hydrides are more brittle and can be readily crushed. Mechanical alloying can also be a great technique for preparing meta-stable alloys of elements that are immiscible even at liquid state.

**[0107]** The meta-stable SS-alloys prepared using the RS or HEHP mechanical alloying methods can be hydrogenated or dehydrogenated in the autoclave and handled in the glove box.

**[0108]** Furthermore, the non-equilibrium processing methods can be not only a way of preparing solid solutions of metals and their hydrides, but also can be an effective method to improve the kinetic properties of these materials owing to the extremely high surface areas and internal defects of nano-sized powders. The microstructure and chemical properties of the materials made by non-equilibrium processing can be significantly different from equilibrium or near-equilibrium materials.

#### Example 5

##### Study Crystal Structures of Hydrogenated Ss-Alloys

**[0109]** Experimentally, the crystal structure of selected SS-alloys and their hydrogenated products (SS-hydrides) can be



analyzed using X-ray diffraction (XRD), transmission electron microscope (TEM), neutron diffraction, nuclear magnetic resonance (NMR), and other techniques. The lattice parameters can be calculated based on XRD patterns to compare with those of pure metals or pure hydrides. High-resolution TEM can be used to characterize the structure of the alloys as functions of alloy compositions. To study the phase transitions, in-situ x-ray synchrotron techniques to monitor the changes during dehydrogenation can be used.

**[0110]** In contrast to XRD, neutron diffraction can locate hydrogen in the structures and refine hydrogen site occupancies during hydrogen loading and unloading of the samples. All patterns of one complete cycle (hydrogen unloading and loading) can be sequentially fitted using the Rietveld refinement program GSAS. Further, more detailed reaction mechanisms and possible intermediate products can also be studied using NMR.

#### Example 6

##### Thermodynamics and Kinetics of Dehydrogenation/ Hydrogenation Reactions

**[0111]** To study the thermodynamics and kinetics of dehydrogenation and hydrogenation reactions, the following tools can be used: thermal-gravimetric analysis (TGA), differential scanning calorimetry (DSC), and Sievert's-type devices such as pressure-composition-temperature analysis (PCT) instrument.

**[0112]** TGA can be a rapid screening tool for measuring dehydrogenation temperature, capacity, and a measure of kinetics based on weight loss. TGA can also be an effective tool for collecting specimen at selected temperatures for studying reaction steps and intermediate products.

**[0113]** DSC can be used to measure enthalpies of reactions or phase transformation. A series of SS-hydrides can be measured by using DSC. The information can also be useful for finding optimum compositions of SS-hydrides with optimum  $\Delta H$  values between 39 and 46 kJ/mol- $H_2$ , which is considered an optimum range for practical hydrogen storage applications.

**[0114]** To study details of thermodynamic and kinetic properties of hydrogenation and dehydrogenation reactions, a Sievert's-type device—HyEnergy PCT Pro2000 can be used. PCT Pro2000 is a highly sophisticated instrument for studying gas solid reactions, especially metal-hydrogen reactions. PCT Pro200 is capable of operating up to 400° C. under 200 bar hydrogen pressure. Three aspects of hydrogen storage properties can be characterized: isothermal equilibrium pressure, isothermal kinetics, and cyclic behaviors. FIG. 10 shows a typical pressure-composition isotherm plot. For a LMSSA, the transition from metal solution phase to SS-hydride phase should follow the solid line in the figure, different from that of traditional metallic hydrides of transition metal or its intermetallic compound in which the initial solubility of hydrogen in the metal phase is higher (as shown by the dashed line). Equilibrium pressure values determined from the isotherm plots at different temperatures can be used to construct van't Hoff plots, which can then be used to calculate activation energies,  $\Delta H$ , and  $\Delta S$  values.

#### Example 7

##### Effect of Doping and Alloying Elements

**[0115]** There are several considerations based on which alloying and additive elements can be chosen including the

effects of an element on: 1). activities of constituents in solid solutions, 2). crystal structure and lattice constants, 3). aid to  $H_2$  dissociation, e.g. transition and noble metals, and 4). possible hydrogen spill over effects, e.g. Pd on carbon support. Suitable alloying elements can include B, C, N, Ti, Ni, Zn, Fe, Co, Pt, K, Ca, and Pd/C. Alloying elements can be incorporated into the alloys during the synthesis process by either high energy mechanical alloying or rapid solidification. Chemical analysis can be done to verify compositions of additives before subjecting the material to hydrogen storage experiments.

**[0116]** To avoid excessively large experimental matrix that may be impossible to complete, we can use TGA as a screening tool. TGA analysis gives us a "starting" temperature of dehydrogenation which usually reflects the changes in thermodynamic as well as kinetic properties of the material. Selected materials that yield significant effects based on TGA analysis can then be characterized in full by using PCT and other more in-depth techniques.

#### Example 8

##### Theoretical Modeling

**[0117]** Theoretical studies can be performed in close correlation with experiments to support experimental efforts by elucidating experimental results and providing theoretical guidelines for further experiments. The main focus can be first-principles calculations, whose results can also be used as input parameters for thermodynamic modeling based on regular solution theory. The first-principles calculations can be performed using the pseudopotential plane-wave method as implemented in the VASP code based on the density functional theory. The generalized gradient approximation of Perdew and Wang and projected augmented wave potentials can be used. The supercell technique can be used to model the SS-alloys with a cell size up to 256 atoms, and the Monkhorst-Pack special k-point scheme can be used to sample the Brillouin zone. Conjugate-gradient algorithm can be used for energy minimization and structure optimization. All the large-scale first-principles calculations can be carried on clusters

#### Example 9

##### Formation Enthalpies of LMSSA and LMSSA Hydrides

**[0118]** Using Li—Mg as an example, one can construct large supercells up to a couple of hundreds of atoms to calculate the cohesive energies of Li—Mg solid solution alloys (SS-alloys), and hence the formation enthalpies in reference to the pure metal phases of Li and Mg, as a function of composition. For a given composition, Mg atoms (as a substitutional solute) can be randomly distributed into the Li lattice sites, in a crystal lattice structure of Li as suggested by the experiment, and multiple configurations can be generated to repeat the calculation of this composition for statistical average to account for the limited system size. Similar calculations can be done for the Li—Mg—H SS-hydride, except the crystal lattice structure is the  $MgH_2$  rutile structure as suggested by the experiment and the formation enthalpies are calculated in reference to LiH and  $MgH_2$ .

**[0119]** One interesting point to note is that for the SS-hydride to assume the structure of  $MgH_2$ , there have to be changes in atomic structure and stoichiometry associated



with replacing an Mg—H<sub>2</sub> unit with a LiH unit to form a “random” solution. On the one hand, if one maintains perfect stoichiometry of (Li,Mg)H<sub>3</sub>, a H-vacancy has to be formed in the original MgH<sub>2</sub> lattice (see FIG. 6), which introduces lattice strain tending to distort the lattice. On the other hand, if one additional H were added to fill the vacancy, the stoichiometry would be broken. Calculations can be used to balance these two factors by energy minimization. The variation in the stoichiometry of the SS-hydrides provides another variable for tuning the H wt %. Especially, the possibility of increasing H concentration (and hence the H wt %) in the solid solution to fill the vacancy so as to stabilize the lattice makes the whole approach even more attractive.

**[0120]** Calculations of other systems (Li—Al, Mg—Al, Li—Al—Mg) can be carried out based on experimental inputs and experience. Thermodynamic analysis can be done to estimate the activity coefficients of metal hydrides (such as LiH and AlH<sub>3</sub>) in the alloyed metal hydrides (such as (Li,Al)H<sub>x</sub>), using the first-principles enthalpy data. For example, based on regular solution theory, the activity coefficient of A in A<sub>x</sub>B<sub>y</sub> solution is  $a_A = x \cdot e^{\Omega y^2 / kT}$ , where  $\Omega = NZ(\Delta h)$ , N is the number of atoms, Z is nearest-neighbor coordination number, and  $\Delta h$  is the formation enthalpy. The dehydrogenation energies of the LMSSA hydrides can be calculated. This can be done by removing H one-by-one from the superlattice of a given LMSSA hydrides such as (Li,Mg)H<sub>x</sub> and calculate the change of energy in reference to LMSSA and H<sub>2</sub>, similar to existing calculations of metal hydrides.

**[0121]** The foregoing detailed description describes the invention with reference to specific exemplary embodiments. However, it will be appreciated that various modifications and changes can be made without departing from the scope of the present invention as set forth in the appended claims. The detailed description and accompanying drawings are to be regarded as merely illustrative, rather than as restrictive, and all such modifications or changes, if any, are intended to fall within the scope of the present invention as described and set forth herein.

What is claimed is:

**1.** A light metal solid solution alloy for reversible hydrogen storage, comprising the light metal solid solution alloy of at least two light metals, M<sub>1</sub> and M<sub>2</sub>, wherein M<sub>1</sub> and M<sub>2</sub> are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si, wherein the alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.

**2.** The light metal solid solution alloy of claim 1, wherein the light metal solid solution further includes at least one additional light metal M<sub>x</sub>, wherein x is from 3 to 6.

**3.** The light metal solid solution alloy of claim 1, wherein the light metal solid solution alloy is selected from the group consisting of Li—Al, Mg—Al, Li—Mg, Li—Mg—Al, Mg—Si and combinations thereof.

**4.** The light metal solid solution alloy of claim 1, wherein the light metal solid solution alloy is metastable.

**5.** The light metal solid solution alloy of claim 1, further comprising a dopant selected from the group consisting of B, Al, C, Si, N, Ti, Ni, Zn, Pt, Sc, Fe, Co, Pd, K, Ca and combinations thereof.

**6.** The light metal solid solution alloy of claim 1, wherein the alloy has a reversible hydrogen weight storage capacity greater than about 5 wt %.

**7.** The light metal solid solution alloy of claim 1, wherein the alloy has a dehydrogenation temperature less than about 400° C.

**8.** The light metal solid solution alloy of claim 1, wherein the alloy has an equilibrium hydrogenation pressure from about 1 bar to about 200 bar.

**9.** A method of forming a light metal solid solution alloy for reversible hydrogen storage, comprising:

a) forming a light metal solid solution alloy of light metals M<sub>1</sub> and M<sub>2</sub>, wherein M<sub>1</sub> and M<sub>2</sub> are different and independently selected from the group consisting of Li, Mg, Al, Na, Be, and Si, wherein the alloy has a hydrogenated state and a dehydrogenated state which are each solid solutions.

**10.** The method of claim 9, wherein each of M<sub>1</sub> and M<sub>2</sub> are each provided as elemental metals.

**11.** The method of claim 9, wherein each of M<sub>1</sub> and M<sub>2</sub> are each provided as metal hydrides.

**12.** The method of claim 9, wherein the forming is accomplished via mechanical alloying.

**13.** The method of claim 12, wherein the mechanical alloying is accomplished using a high energy high pressure planetary milling machine.

**14.** The method of claim 9, wherein the forming is accomplished via rapid solidification.

**15.** The method of claim 14, wherein the rapid solidification is centrifugal atomization.

**16.** The method of claim 9, wherein the forming further comprising including a doping element with the light metals.

**17.** The method of claim 9, wherein the alloy has a grain size from about 5 nm to about 15 nm.

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