Hydrogen Trapping in Mg_2Si and Al_7FeCu_2 Intermetallic Compounds in Aluminum Alloy: First-Principles Calculations

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From first-principles calculations, we estimated the trapping energy of hydrogen atom at the interstitial site of perfect crystals of Mg_2Si and Al_7FeCu_2 intermetallic compounds in the aluminum matrix. We found that Al_7FeCu_2 trapped hydrogen atoms strongly, whereas Mg_2Si did not. The highest trapping energy in Al_7FeCu_2 is 0.56 eV/atom. We also found that the density of hydrogen trapping can be increased up to about 13 atoms/nm³ while keeping high trapping energy of about 0.40 eV/atom. We inferred that the Al_7FeCu_2 phase might remove hydrogen from the aluminum matrix, hence, preventing hydrogen embrittlement of aluminum alloy. [doi:10.2320/matertrans.MT-M2020201]

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1. Introduction

High strength 7xxx aluminum alloy is known for its low resistance to stress corrosion cracking and hydrogen embrittlement.^{1–3)} Brittle fracture is caused by hydrogen along grain boundaries and crystal planes. The removal of hydrogen atoms from the aluminum lattice in some way is one of the effective methods to prevent hydrogen embrittlement.

Aluminum alloys contain some precipitates and second phases consisting of intermetallic compounds. Recently, we discovered that MgZn_2 , referred to as η phase, does not trap hydrogen atom inside its crystal lattice but traps hydrogen atom on its coherent interface with aluminum matrix.^{4,5)} The trapping energy was about 0.3–0.4 eV/atom. Therefore, precipitates and second phases may affect the distribution of hydrogen atoms in aluminum alloy.

η - MgZn_2 are aged precipitates ranging from a few nanometers to several tens of nanometers in size. On the other hand, Mg_2Si and Al_7FeCu_2 are second phase particles dispersed in aluminum alloy with size on the order of a few micrometers. These are the major second phases observed in the 7xxx alloy.^{6,7)} There have been minimal reports on the analysis of hydrogen trapping by the second phase particles.

In this study, we employed first-principles calculations to investigate the strength and density of hydrogen trapping inside the crystal lattice of second-phase Mg_2Si and Al_7FeCu_2 intermetallic compounds in the aluminum matrix. We found that Al_7FeCu_2 was able to absorb a large number of hydrogen atoms strongly at its interstitial sites in the unit cell, while Mg_2Si did not.

2. Calculations

We conducted first-principles calculations using the density-functional theory framework as implemented in the Vienna Ab initio Simulation Package (VASP) using the Projector-Augmented Wave method with Perdew-Burke-Ernzerhof exchange-correlation (PAW-PBE) potentials.^{8–11)} The Monkhorst-Pack algorithm¹²⁾ was selected for the Brillouin-zone k-point samplings. A plane-wave energy cutoff of 325 eV was used with a first-order Methfessel-Paxton smearing scheme, employing a smearing parameter of 0.2 eV. The total energy converged to 10^{−6} eV in all the calculations. The relaxed atomic configurations were obtained by the conjugate gradient method in which the search terminated when the forces on all atoms were below 0.01 eV/Å. In some cases, the zero-point energy (ZPE) of hydrogen was calculated. The solution energy of hydrogen atom at a tetrahedral (T) site in the face-centered cubic aluminum lattice was calculated by using a 4 × 4 × 4 supercell (256 atoms/cell) with a 3 × 3 × 3 k-point sampling.

The experimental crystal structure parameters of the Mg_2Si ¹³⁾ and Al_7FeCu_2 ¹⁴⁾ intermetallic compounds are used as initial parameters and then fully relaxed in our first-principles calculations. The sampling k-point mesh of 3 × 3 × 3 (6 × 6 × 3) was used for supercell containing 96(80) atoms for Mg_2Si (Al_7FeCu_2).

The possible trapping sites of the hydrogen atom are shown in Fig. 1. Voronoi tessellation analysis found these possible interstitial sites in the crystal of the Mg_2Si and Al_7FeCu_2 intermetallic compounds. Crystal structures were visualized by using VESTA (Visualization for Electronic and Structural Analysis) software.¹⁵⁾ First, the vertex of Voronoi polyhedron was modeled to be a possible trap site for a hydrogen atom. We call this a vertex site. Second, the center point of each plane on Voronoi polyhedron was also selected to be a possible trap site. However, the point between the two

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Fig. 1 Crystal structures and possible trap sites for a hydrogen atom (two kinds of small spheres having bright and dark colors indicated by H). (a) Mg_2Si . (b) Al_7FeCu_2 . Bright and small spheres are vertex sites, while dark and small spheres are midpoint sites. See text.

nearest neighboring atoms was ignored because there was almost no space for hydrogen. This second-type point corresponds to an interstitial octahedral site in a simple bcc lattice, which is a midpoint between the pair of second nearest neighboring atoms. For this reason, we call this point a mid-point site.

The method of calculation for the hydrogen trapping energy is the same as that employed in our previous paper⁴⁾ for $\eta\text{-MgZn}_2$ precipitates. In our method, the definition of inherently negative trapping energy (E_{trap}) is the energy change by the migration of dissolved hydrogen atom from a tetrahedral site in aluminum (Al) matrix consisting of 256 atoms to a possible trapping site in the perfect crystal of Mg_2Si (or Al_7FeCu_2) compound consisting of 96 (or 40) atoms. An equation is shown as

$$E_{\text{trap}} = E_{\text{tot}}(\text{H} + \text{compound}) - E_{\text{tot}}(\text{compound}) - \{E_{\text{tot}}(\text{H} + 256\text{Al}) - E_{\text{tot}}(256\text{Al})\}. \quad (1)$$

Here, the total energy (E_{tot}) of the unit cell is calculated from first-principles. The trapping energy (E_{trap}) is an inherently negative value. However, the trapping energy is usually referred to as the positive value ($-E_{\text{trap}}$).

3. Calculated Results

3.1 No trap sites in Mg_2Si

The conventional unit cell of Mg_2Si is small, with only 12 atoms. Hence, the hydrogen trapping energy was calculated using a $2 \times 2 \times 2$ supercell (96 atoms/cell). Possible trap sites for hydrogen atom were searched for, and then seven kinds of sites were found. The trapping energy of hydrogen ($-E_{\text{trap}}$) was calculated by placing one hydrogen atom at each site in the supercell.

As a result of calculations, we were not able to find any site for a hydrogen atom to be trapped in the supercell of Mg_2Si . Figure 2 shows the calculated trapping energies at the two sites. In both cases, the trapping energy ($-E_{\text{trap}}$) shows negative values, which means that the hydrogen atom is unstable in the lattice of Mg_2Si compared to the solution state of a hydrogen atom at a tetrahedral site in the aluminum matrix.

3.2 Strong trap sites in Al_7FeCu_2

The conventional unit cell of Al_7FeCu_2 contains 28 Al, 4 Fe, and 8 Cu atoms, a total of 40 atoms. This unit cell is large enough. Thus, a larger size of the supercell was not necessary for the calculations of hydrogen trapping energy. As shown in Fig. 1(b), the Voronoi tessellation analysis found many possible trap sites for a hydrogen atom. There are about 61 sites in total; this number is not the exact number of inequivalent sites but the reduced number of sites by using point group symmetry for saving computational time.

The considerable size of hydrogen trapping energy ($-E_{\text{trap}}$) was obtained in our calculations. As shown in Fig. 3, the trapping energies in Al_7FeCu_2 are 0.56 eV/atom, 0.46 eV/atom, and 0.41 eV/atom for the site I, II, and III, respectively. According to our previous papers, hydrogen trapping energy was about 0.2 eV/atom on the grain boundaries of aluminum,⁵⁾ and 0.3–0.4 eV/atom on the coherent interface between precipitate ($\eta\text{-MgZn}_2$) and matrix (Al).⁴⁾

The ZPE of the hydrogen atom was also calculated in some cases. It was in the range of 0.11–0.20 eV/atom. At the tetrahedral site in the aluminum lattice, the ZPE of hydrogen atom was about 0.16 eV/atom.¹⁶⁾ Therefore, the ZPE correction energy was within ± 0.05 eV/atom, which is small

(a) Site I

(0.25, 0.13, 1.0)

– 0.20 eV/atom (No trapping)

(b) Site II

(0.5, 0.08, 0.08)

– 0.31 eV/atom (No trapping)

Fig. 2 Interstitial sites where hydrogen atoms are relatively stable in the Mg_2Si lattice. However, the hydrogen atoms at these sites are still less stable than those in the aluminum lattice. The trapping energies are negative, which means that these sites cannot trap hydrogen atom from the aluminum matrix. Relative values of x, y, and z coordinates (from 0 to 1) are shown in the parenthesis.

(a) Site I

(0.50, 0.00, 0.19) 0.56 eV/atom

(b) Site II

(0.18, 0.93, 0.22) 0.46 eV/atom

(c) Site III

(0.5, 0.5, 0.09) 0.41 eV/atom

(d) Site IV (Unstable)

(0.0, 0.5, 0.25) 0.40 eV/atom

Fig. 3 Trapping sites' positions (x, y, z) and energies ($-E_{\text{trap}}$) without ZPE correction in the unit cell of Al_7FeCu_2 . Atomic distances (nm) around the hydrogen atom after relaxation are shown. Site IV is not a stable trapping site because its ZPE component has an imaginary one. The sites near the cell boundary plane are shown twice because of periodic boundary conditions.

Fig. 4 Multiple hydrogen atoms' trapping and their energies in the unit cell of Al_7FeCu_2 . Here, the definition of E_{trap} is extended for more than one hydrogen atoms in the unit cell. Up to eight hydrogen atoms occupy all of the sites I (Fig. 3(a)) in the unit cell. Then, more hydrogen atoms up to twelve occupy the sites near iron (Site II as in Fig. 3(b)). Most of the trapped hydrogen atoms are placed near the cell boundary plane and thus shown twice because of periodic boundary conditions.

compared to the obtained trapping energies. As shown in Fig. 3(d), the site IV is not a trap site but a saddle point site for a hydrogen atom because an imaginary component appeared in its ZPE.

3.3 Multiple hydrogen trapping in Al_7FeCu_2

It is interesting to know how much hydrogen atoms can be trapped in the Al_7FeCu_2 lattice. In our calculations, the number of hydrogen atoms in the unit cell of Al_7FeCu_2 was gradually increased to calculate the trapping energy of the whole hydrogen atoms.

Figure 4 shows the calculated trapping energy of the total hydrogen atoms when the hydrogen atoms are multiply trapped in the unit cell of Al_7FeCu_2 . As a result, crystallographically equivalent eight sites (the site I) in the cell were gradually filled with hydrogen atoms. We obtained this result by paying attention to the arrangement of the hydrogen atoms to maximize the energy gain. As a result, the energy gain obtained by each trapped hydrogen atom decreases with increasing the total number of trapped hydrogen atoms. The trapping energy of the firstly trapped hydrogen atom is 0.56 eV/atom, while that of an eighth hydrogen atom is 0.40 eV/atom, as shown in Fig. 4. However, the trapping energy of 0.40 eV/atom is still higher than that of grain boundary⁵⁾ of about 0.2 eV/atom, and that of Al–MgZn₂ coherent interface of about 0.3–0.4 eV/atom. The cell volume is expanded by 2.7%, with eight trapped hydrogen atoms.

From the ninth hydrogen atom, four equivalent interstitial sites (site II) were found to trap hydrogen atoms, as shown in Fig. 4. In this stage, site III cannot trap hydrogen atom because the distance between sites I and III are so close

(about 0.2 nm) that hydrogen atoms at sites I and III repel each other. The hydrogen atoms can be more stable if they are trapped at site II, which is sufficiently far from the site I. However, the trapping energy of the ninth hydrogen atom is only 0.16 eV/atom, as shown in Fig. 4, which is considerably lower than the 0.56–0.40 eV/atom.

The above result infers that the absorption of hydrogen atoms may be almost saturated at eight hydrogen atoms in the unit cell of Al_7FeCu_2 (40 atoms/cell). The trapping energy of 0.16 eV/atom is smaller than the hydrogen trapping energy along grain boundaries (0.2 eV/atom).⁵⁾ The crystal lattice of Al_7FeCu_2 is also considerably expanded by eight trapped hydrogen atoms; the volume expanded by 4.6%.

The behavior of multiple hydrogen trapping in the crystal lattice of Al_7FeCu_2 is summarized as follows. First, the central point inside a tetrahedron consists of four aluminum atoms (the site I) preferentially traps hydrogen atom, as shown in Fig. 4(a). Second, the site II traps a hydrogen atom, where a chemical bonding with Fe forms, as shown in Fig. 4(b). Hydrogen trapping in the vicinity of Cu was not easy to realize, probably because Cu has an electronic structure of a closed shell of fully occupied 3d orbitals.

4. Discussion

In our calculations, we made several essential assumptions to reduce computational cost. First, the crystal structures of the compounds Mg_2Si and Al_7FeCu_2 are assumed to be completely stoichiometric. However, it is not known whether the crystal structure of the second phase particle is almost stoichiometric or not in the aluminum matrix. Furthermore, we assumed that there was no crystallographic defect in these

compounds. The vacancy-type defect must be a stable trap site for hydrogen. However, we did not consider such defects for simplicity.

Even with our approach to finding hydrogen trap sites by using the Voronoi tessellation technique, no one can deny that there may be missing sites for hydrogen trapping. At present, however, this is considered a practical approach in the situation where the available computation time is limited. In the future, ideally, we should calculate the three-dimension mapping of hydrogen trapping energy at all possible interstitial positions on a sufficient resolution mesh points in an interstitial space of the unit cell.

We cannot calculate the ZPE of hydrogen atoms at multiple trapping states because of the shortage of computational time. Therefore, the stability of hydrogen atoms at a multiply trapping state is yet to be known. The migration barrier energy of hydrogen atoms between trap sites is also of interest, which is a future study.

5. Conclusions

We investigated the possibility of hydrogen trapping at interstitial sites in the perfect crystal lattice of Mg₂Si and Al₇FeCu₂ intermetallic compounds in the aluminum matrix by first-principles calculations. Any interstitial site in the Mg₂Si lattice was not able to trap hydrogen atom. On the other hand, the Al₇FeCu₂ lattice had some inequivalent interstitial sites that can trap hydrogen atom with high trapping energies such as 0.56, 0.46, and 0.41 eV/atom. The high trapping density of hydrogen atoms of about 13 atoms/nm³ would be possible while maintaining the trapping energy of each hydrogen atom at 0.40 eV/atom or more.

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REFERENCES

- 1) K. Shimizu, H. Toda, K. Uesugi and A. Takeuchi: *Metall. Mater. Trans. A* **51** (2020) 1–19.
- 2) H. Su, H. Toda, K. Shimizu, K. Uesugi, A. Takeuchi and Y. Watanabe: *Acta Mater.* **176** (2019) 96–108.
- 3) H. Toda, T. Hidaka, M. Kobayashi, K. Uesugi, A. Takeuchi and K. Horikawa: *Acta Mater.* **57** (2009) 2277.
- 4) T. Tsuru, M. Yamaguchi, K. Ebihara, M. Itakura, Y. Shihiara, K. Matsuda and H. Toda: *Comput. Mater. Sci.* **148** (2018) 301–306.
- 5) M. Yamaguchi, K. Ebihara, M. Itakura, T. Tsuru, K. Matsuda and H. Toda: *Comput. Mater. Sci.* **156** (2019) 368–375.
- 6) T. Manaka and G. Itoh: *J. JILM* **67** (2017) 67–71.
- 7) H. Su, T. Yoshimura, H. Toda, Md.S. Bhuiyan, K. Uesugi, A. Takeuchi, N. Sakaguchi and Y. Watanabe: *Metall. Mater. Trans. A* **47** (2016) 6077–6089.
- 8) G. Kresse and J. Hafner: *Phys. Rev. B* **47** (1993) 558–561.
- 9) G. Kresse and J. Furthmüller: *Phys. Rev. B* **54** (1996) 11169–11186.
- 10) J.P. Perdew, K. Burke and M. Ernzerhof: *Phys. Rev. Lett.* **77** (1996) 3865–3868.
- 11) P.E. Blöchl: *Phys. Rev. B* **50** (1994) 17953.
- 12) H.J. Monkhorst and J.D. Pack: *Phys. Rev. B* **13** (1976) 5188–5192.
- 13) Y. Noda, H. Kon, Y. Furukawa, N. Otsuka, I.A. Nishida and K. Matsumoto: *Mater. Trans., JIM* **33** (1992) 845–850.
- 14) M.G. Bown and P.J. Brown: *Acta Crystallogr.* **9** (1956) 911–914.
- 15) K. Momma and F. Izumi: *J. Appl. Crystallogr.* **44** (2011) 1272–1276.
- 16) C. Wolverton, V. Ozolins and M. Asta: *Phys. Rev. B* **69** (2004) 144109.