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[1] **R:** Document, report (excluding the periodic and final reports).
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Table of Content

1 Introduction

The primary objective of this report is to explain the investigation carried out using density functional theory (DFT) to identify suitable Mg-anodes based on Mg-alloys for rechargeable magnesium batteries. This task contributes to the project sub-objective 2 (SO2) which aims to identify the alloying elements which enhance the ductility of Mg anode, as well as its dissolution/deposition efficiency based on DFT calculations. ***The public version of this deliverable will be released as soon as a manuscript related to the work presented here is accepted***.

Magnesium based rechargeable batteries (RMB) are considered as a promising alternative to lithium-ion batteries. Magnesium metal is an interesting anode material due to its abundance in the earth, high volumetric capacity and its sustainability. However, the passivation layer formed at the electrode surface in contact with the ordinary electrolytes hinders the diffusion of Mg-ions, and it negatively impacts the coulombic efficiency [1]. To bypass this drawback, Aurbach et al. reported a breakthrough by proposing organohaloaluminate based electrolytes in ethereal solutions [2]. Further several studies are focusing on developing new generation electrolytes suitable for RMB.

Another potential solution to overcome this limitation is to use metals that form alloys with magnesium as anode material. Several studies were reported on systems such as Bi, Sn, Sb, In, Bi-Sb to use as the anode in magnesium ion batteries (MIB) [3, 4, 5, 6]. Even though reversible magnesiation is possible with these materials, they face some challenges such as capacity loss at higher C-rate, sluggish Mg-ion kinetics and pulverization of electrode due to volume expansion [1].

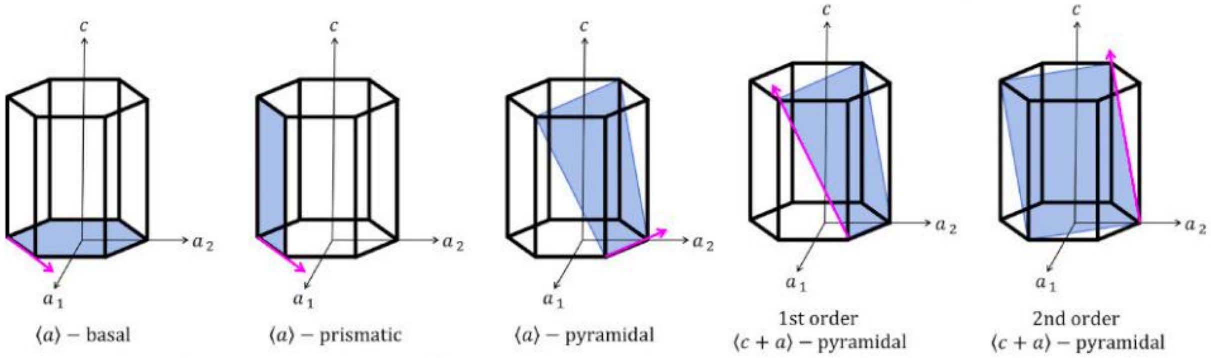
Magnesium should be used as the anode in order to exploit its capability in terms of energy density completely. But magnesium exhibits poor ductility due to their hexagonal crystal structure. Therefore, its workability is limited in room temperature, and this creates difficulty while forming into foils. Alloying with suitable elements can improve the ductility of magnesium (an in-depth description can be found in deliverable D2.1). In section 2, it discusses stacking fault energy as a descriptor for ductility mechanism in magnesium. Based on this descriptor, it shortlisted the alloying elements which improve the ductility of magnesium. Then, DFT calculations have been performed to filter the elements which segregate to the bulk instead of to the surface. It was done in order to obtain those Mg-alloys with a surface similar to pure Mg-anode.

2 Descriptor for ductility mechanism

The brittleness of hexagonal close-packed (hcp) Mg is on account of insufficient independent slip systems needed for general deformation. According to Von-Mises criterion, five independent slip modes are required for a deformation [7]. But hcp-Mg has only two basal slip systems available at room temperature. The possible slip systems in hcp crystal are illustrated in **Figure 1** [8], and the independent deformation modes are listed in **Table 1** [9]. Basal <a> slip systems cannot accommodate the strain along c-axis of the crystal [9, 10]. Therefore non-basal slips particularly <c+a> pyramidal slip planes need to be activated to accommodate the strain along c-axis. From

Table 1, it is clear that activation of <c+a> pyramidal slip itself can provide five independent slip modes. Curtin et al. showed that <c+a> dislocations are metastable even they formed in Pure-Mg [11].

Alloying with suitable elements can activate and stabilize non-basal dislocation and slip systems. Alloying elements activate the non-basal dislocations by reducing the stacking fault energy (SFE). The plausible explanation for this explanation is that stacking fault can act as nucleation source for <c+a> dislocations. And this nucleation of <c+a> dislocations is a critical step in providing slip modes out of basal plane. Thus the reduction in stacking fault energy can be used as the descriptor for the ductility mechanism in hcp-Mg [12].



$\langle a \rangle$ − basal

$\langle a \rangle$ − prismatic

$\langle a \rangle$ − pyramidal

1st order $\langle c + a \rangle$ − pyramidal

2nd order $\langle c + a \rangle$ − pyramidal

Figure 1: *Possible slip systems in hexagonal system* [8]

Direction	Plane	Number of independent modes
<a>	Basal Slip	2
	Prismatic slip	2
	Pyramidal Slip	4
<c+a>	Pyramidal slip	5
Twinning		0-5

Table 1. *Independent Modes of Deformation in hcp crystals* **[9]**

3 Methodology and computational details

Initially, based on the literature, binary alloying elements which reduce the stacking fault energies on alloying were identified as suitable dopants to enhance the ductility of Mg [13]. Then, the preference to segregate towards bulk or surfaces were investigated based on the energy of formation (E_f) calculated using DFT. Solutes which prefer to be in the bulk are suitable elements thus, the electrode's surface, which is in contact with the electrolyte, will be similar to that of pure-Mg.

The three most favorable surfaces in hcp-Mg are (0001), (10-10) and (10-11). It used 96-atom supercells with one dopant on each of the two surfaces to obtain a lower concentration of the dopants (~ 2 at %). The lesser value of the E_f of dopant in bulk compared to dopant in surfaces indicates that solute prefers to go into the bulk. Also, the maximum E_f of bulk is chosen as 0.05 eV, since elements with higher E_f is less favorable to form alloy at that concentration. Therefore it can discard these systems.

The energy of formation (E_f) for the bulk and surfaces of the alloys were calculated using the equation below:

$$E_f^{bulk/surface} = \frac{E_{Mg+X}^{bulk/surface} - E_{Mg}^{bulk/surface} - nE_X + nE_{Mg}}{n}$$

where $E_{Mg}^{bulk/surface}$ is the energy of pure Mg, $E_{Mg+X}^{bulk/surface}$ is the energy of structure with alloying element X, E_X is the energy per atom of X, E_{Mg} is the energy of pure Mg per atom and n is the number of dopants.

Formation energies were determined by first-principles calculation based on DFT using the Vienna Ab initio Simulation Package (VASP) [14, 15]. The Perdew-Burke-Ernzerhof (PBE) parameterized generalized gradient approximation (GGA) functional was employed to describe the exchange and correlation effects [16] and, the projector augmented wave (PAW) [17] method was used to account for the core-valence interaction. A plane wave basis set with cut-off energy of 520 eV is used for the calculations. Brillioun zone is integrated with the k-point mesh generated using the Monkhorst-Pack scheme with a k-point density of 4.5 per A^{-1}.

4 Results and discussion

Binary alloying elements which reduce the stacking fault energies on alloying are identified as suitable dopants to enhance the ductility of Mg. The solutes chosen from the literature based on the above criteria are Al, Ba, Bi, Ca, Ce, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, In, K, La, Lu, Na, Nd, Pb, Pr, Rb, Sc, Sm, Sn, Sr, Ta, Ti, Tm, Y, Yb, Zn and Zr [13].

Then the preferred segregation of the solute is analyzed based on the energy of formation (E_f) calculated using DFT. For better visualization, E_f of bulk and surface of Mg-alloys are shown in two figures with different scale of energies (**Figures 2a** and **2b**). The formation energies of the Mg-alloys with Al, Ga, Zn and rare earth elements are illustrated in **Figure 2a**. And the E_f of Mg-alloy with rest of the elements is shown in **Figure 2b**. Aluminium and most of the rare earth elements (Sc, Y, Dy, Er, Gd, Ho, Lu, Nd, Pr and Tm) preferred to segregate towards the bulk, and their bulk formation energies are less than 0.05 eV. Among the above list, Sc, Y and Gd show negative E_f for the bulk. The 3B periodic table group elements Y and Sc have the most negative bulk formation energy among the elements which preferred to segregate into the bulk.

Schloffer et al. studied Mg-1.55 wt% Gd, Mg- 1.63 wt% Zn and Mg-1.02 wt% Zn-1.01 wt% Gd as anodes in APC electrolyte and reported that the addition of the alloying element does not have any adverse effect on the anode performance. They also observed that Mg1.6Zn is more passivating than the other alloys [18]. This observation agrees with the formation energies calculated for Zn. Even though the bulk E_f is lower than the E_f for (0001)-surface, the other two surfaces have the lowest formation energies. The similar trend can be observed for Ga as well. Among the rare earth elements La, Ce, Eu and Yb are the elements which did not satisfy our criteria for ductile Mg-alloy anode.

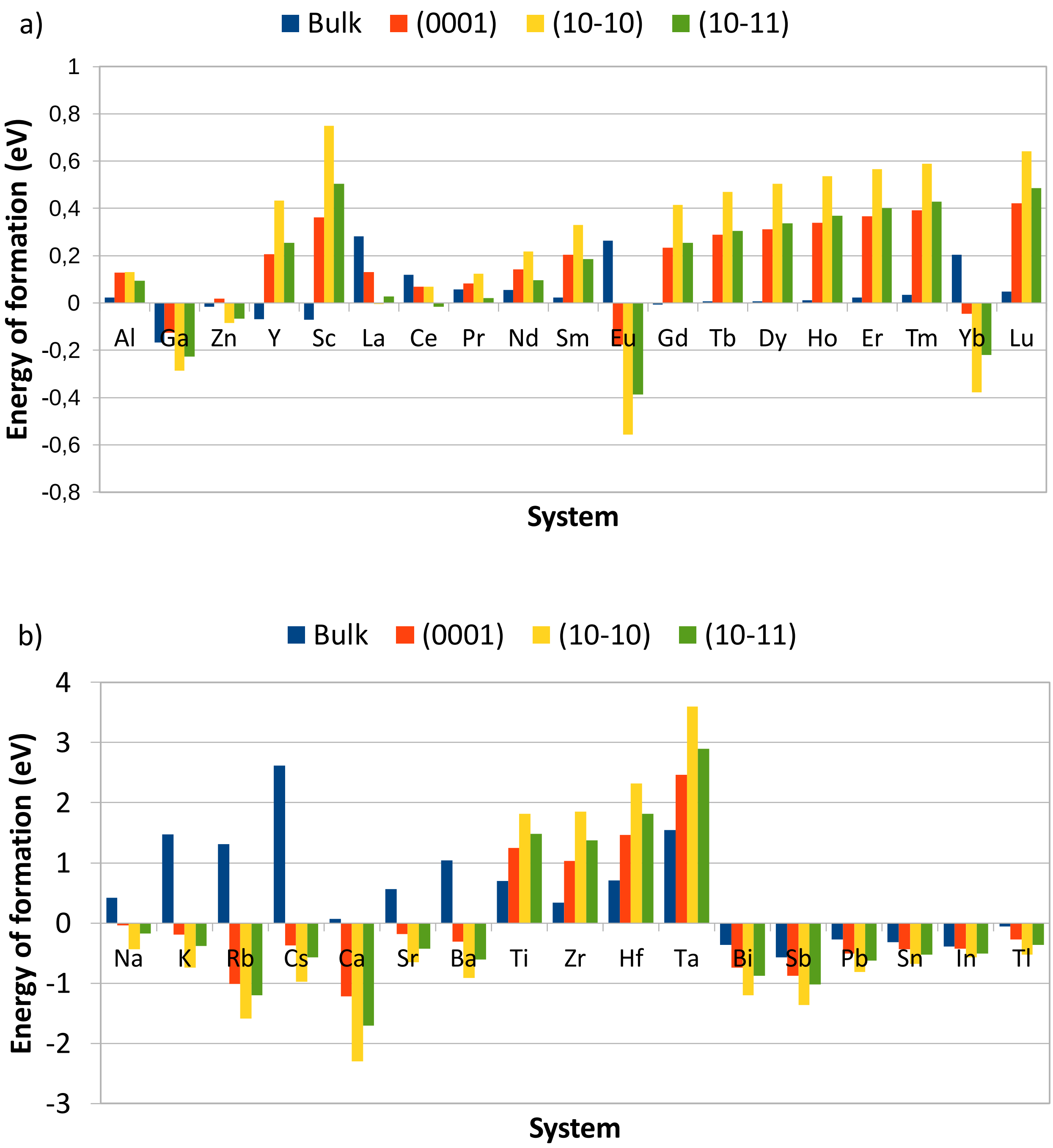


Figure 2 : *Energy of formation of Mg-alloys (Note that the y-axis scale is different for both figures)*

The 1A and 2A periodic table group elements show a similar trend for the formation energies. One of the reasons for the high bulk E_f may be their bigger atomic size. Even though the bulk E_f of the Ti, Zr and Hf are lower than the E_f of surfaces, their value of bulk formation energies is very high. These elements are known to be less soluble in magnesium [19]. For Bi, Sb, Pb, Sn, In and Tl the alloy formation is favorable, but the solute strongly preferred to segregate to the surface.

5 Summary

Two criteria were defined for the selection of Mg-alloy anode with improved ductility.

1. The first criterion is based on stacking fault energy. The ductility of Mg can be enhanced by high activity of pyramidal <c + a> dislocations as slip modes out of the basal plane. Intrinsic stacking fault acts as a source for nucleation for the <c + a> dislocations. Therefore the dopants which reduce the stacking fault energy when alloying with hcp Mg were selected from the literature.
2. The second criterion refers to the segregation of the alloying elements to the bulk so that the surface becomes Mg rich. Consequently, the surface of Mg-alloy becomes similar to that for pure Mg-anode.

Based on these criteria, ***it strongly recommends Y, Sc and Gd to be used as additives for ductile Mg-alloy anode.*** Also, ***Al and other rare elements such as Dy, Er, Ho, Lu, Nd, Pr and Tm have showed promising results.***

6 References

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