

Article Quantum Behaviour of Mg and Mg-Al-Zn Microstructure

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Abstract: Magnesium is an essential element because of its many beneficial properties and advantages over other metals, including its lack of risk to people's health and its reasonable cost. However, Mg has several disadvantages, one of which is its high corrosion rate. This work analysed magnesium alloy characteristics and quantum behaviour, including band structure, molecular orbital, and corrosion behaviour in the presence of water. Magnesium was characterised by density functional theory software using CASTEP and Dmol3. Results showed no Mg band structure displays a conductive Fermi level of 8.85 eV. Curvature studies revealed that Mg has strong curvature and electron mobility. The density of state (DOS) of Mg-Al-Zn changes with Al and Zn alloy atoms, and the electron density increases to -7.5 eV compared with pure Mg. HOMO–LUMO analysis elucidated that Mg-Al-Zn* has a large gap (0.419 eV), leading to its stability and low chemical reactivity. This study analysed the properties of Mg and then examines the effect of corrosion on Mg alloys using DFT at different element positions. Corrosion analysis indicated that Mg-Al-Zn has the highest activation energy, implying that its corrosion is less likely than that of other alloys.

Keywords: Mg microstructure; quantum behaviour; band gap; molecular orbital; corrosion; density functional theory

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1. Introduction

Magnesium (Mg) is the eighth most plentiful element in the crust of the Earth. Many resources are available to address the usage of Mg alloys in various engineering fields [1–4]. Mg alloys have the highest strength-to-weight ratio among structural alloys [5–7]; however, their balance of properties (other than strength) is still the subject of intensive research. These attributes include corrosion, ductility, and creep resistance. Mg alloys have excellent castability, allowing them to be fabricated as complex shapes via procedures with fast production rates, such as high-pressure die casting [8,9]. Depending on the shape, items made of Mg can be die cast up to 50% quicker than their aluminium (Al) counterparts. Compared with polymers, Mg alloys have superior mechanical properties and higher thermal conductivity. Additionally, Mg may be recycled in whole, which is not the case for polymers.

Despite the numerous benefits and low cost of Mg (especially its cost per unit volume), the utilisation of Mg alloys is still restricted. The corrosion resistance of Mg is one of the primary 'Achilles heels' that limit the usage of Mg alloys [10–12]. Improving one attribute of Mg alloys, such as increasing its creep resistance by loading rare earth elements, makes corrosion even worse [13,14]. Similarly, the increased strength of Mg alloys is typically obtained at the expense of their resistance to corrosion. Therefore, corrosion is the most common denominator that demands urgent attention. Other issues include the burning of Mg and the rapid oxidation of molten Mg when exposed to air. The pyrophoric nature of Mg powders somewhat restricts the use of Mg alloys and complicates their fabrication. These issues can only be resolved in foundries with adequate environmental control.

In terms of negative standard electrode potential, Mg is more negative (-2.37 V vs. SHE) than Al (-2.31 V vs. SHE) and zinc (Zn) (-1.25 V vs. SHE). Theoretically, Mg might possess a strong ability to transfer electrons and discharge activity for power generation [15–17]. However, the Faradic capacity of Mg ($2.205 \text{ A} \cdot \text{h/g}$) is lower than that of lithium ($3.862 \text{ A} \cdot \text{h/g}$) and Al ($2.980 \text{ A} \cdot \text{h/g}$) and significantly greater than that of Zn ($0.820 \text{ A} \cdot \text{h/g}$) [15]. This feature is due to the low specific weight and high power and energy density of Mg and may affect its behaviour in metal solutions with positive electrochemical potential. This characteristic adds value to Mg metal, allowing it to generate electricity due to the potential difference between the electrodes, and even to produce hydrogen.

The interaction of magnesium microstructure, and doping with other atoms using the density functional theory (DFT) technique, has been widely studied among researchers. Würger et al. [18] studied the first-principle analysis of the charge transfer in magnesium corrosion by combining water molecules in their structure. The study did not show any firm results on the energetic and electronic states of the reaction. Nezafati et al. [19] used a DFT study on the water molecule adsorption and the surface dissolution behaviour of Mg alloys by adding Al, Zn, Ca, and Y atoms. Generally, they found that the relative electrode potential shift of Mg-Y alloys is positive whereas that of other alloys was negative. Nezafati et al. [20] also applied a DFT calculation to study the hydrolysis behaviour of degradable Mg/Mg alloys, resulting in a good explanation of water adsorption and the stability of the corrosion surface. In addition, Ma et al. [21] studied the DFT calculation of Al-Cu-Mg alloys, which led to stability effects during the addition of specific atom amounts in those alloys. Zhou et al. [22] studied the properties of Li, Al, and Cd-doped Mg alloys using a first-principle calculation to calculate the cohesive energy and its electronic structure. The study showed that Mg-Al alloy has the lowest cohesive energy and is the most stable alloy. The DFT calculation was also used by Carrasco et al. [23] and Chen et al. [24] to illustrate the structure of water over metal surfaces; results showed that strong adsorption of the water molecule on the metal surface leads to weaker hydrogen bonding among the molecules. Kolb et al. [25,26] and Calle-Vallejo et al. [27] also applied DFT calculations on stepped Pt surfaces. They showed that surfaces with a lower coordination number exhibit a higher tendency to adsorb water molecules. Peköz et al. [28] observed a similar adsorption behaviour for water clusters on both flat and stepped transition metal surfaces. Greeley and Norskov [29] and Strasser et al. [30] studied the thermodynamic behaviour of dissolution in the alloy surfaces of transition metals based on periodic DFT calculations.

This work investigated the characteristics, band structure, and distribution of density of states (DOS) of Mg. Testing for corrosion in the presence of water is also carried out to determine how the presence of water affects the process. This article could be helpful in a range of applications, such as for the medical industry, which utilises Mg, and for the study of energy and hydrogen production. The effect of Mg corrosion on sodium chloride solution was also analysed to provide a reference for the production of electricity using air–Mg fuel cells. Corrosion plays an important part in each of these study fields; thus, controlling the degradation of the material is necessary for the implementation of this strategy. Many different approaches, including surface coatings and alloying, can be adopted to protect Mg from corrosion.

2. Materials and Methods

Density functional theory (DFT) calculations were performed using the CASTEP and Dmol3 modules in the Materials Studio[®] software package (version 8.0 BIOVIA Inc.). The most stable electronic state was found by geometry optimisation. The Mg lattice structure was taken from the existing model (with space group of P63/mmc; lattice parameter of a = 3.2094 A, b = 3.2094 A and c = 5.2105 A; and angle α = 90.0° β = 90.0°, and γ = 120.0°) as shown in Figure 1 [31]. The structure was expanded using a 3 × 3 × 2 supercell, and then Al and Zn atoms were added randomly (at the top, middle, and bottom of the Mg atom arrangement) to obtain Mg-Al-Zn alloys with different atom arrangements. Water molecules were added during the reaction calculation on top of the pure Mg and Mg-Al-

Zn alloy structure as a reactant, while the product was built as a magnesium hydroxide molecule and hydrogen gas based on Equations (12)–(15).



Figure 1. Mg lattice structure.

Firstly, the band structure of Mg was estimated using CASTEP (GGA-PBE functional with ultra-fine energy cut-off and SCF tolerance, fine gamma k-point set, $2 \times 2 \times 1$, and OTFG ultrasoft pseudopotentials). A DOS graph for each Mg and Mg-Al-Zn structure was obtained by running Dmol3 with the PBE function in the GGA scheme with a Fermi smearing value of 0.005 Ha (1 Ha = 27.2114 eV) to optimise the structure, and a DND basis set with a basis file of 3.5 4.4 and fine k-point set ($2 \times 2 \times 1$). The data are compared in the Section 3. The transitional state of the reaction between the metals and water molecules was calculated using the same Dmol3, PW91 functional, and complete LST/QST optimisation (TS search) with a Fermi smearing value of 0.005–0.1 Ha (1 Ha = 27.2114 eV), a DND basis set with a basis file of 4.4, a medium k-point set ($1 \times 1 \times 1$), and RMS convergence of 0.01 Ha/Angstrom to find its activation energy. The highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO) energy was calculated (by setting nonperiodic models and choosing the gamma kpoint of the structure) and diagrammed for each metal with a grid interval of 0.25 A and border of 3.0.

3. Results and Discussions

In this section, the current findings are integrated with previous results. This section is divided into three different parts: band structure, HOMO–LUMO analysis, and corrosion study. The band structure is discussed from three different perspectives: Brillouin zone, band gap, and DOS analysis.

3.1. Band Structure

3.1.1. Brillouin Zone

The Brillouin zone is an important concept in studying the electrical structure of solids. A key idea in solid-state physics is the Brillouin zone, which is crucial to comprehending the fundamental concepts of electronic energy bands on a theoretical level. The Wigner–Seitz primitive cell of the reciprocal lattice is referred to as the first Brillouin zone. These points comprise the collection of points in the reciprocal space that are closest to K = 0 compared to any other reciprocal lattice point. The second Brillouin zone is the collection of points that may be reached from the first zone by merely straddling one Bragg plane. The *n*th Brillouin zone is the collection of locations that may be reached from the origin by crossing at least n - 1 Bragg planes, according to a generalisation of this definition. Figure 2 shows the Brillouin zone of a basic Mg structure that is considered in calculating the band structure.

The G, F, Q, and Z points are considered to comprise the simplest path, which was chosen for band structure analysis.



Figure 2. Brillouin zone of Mg structure for band structure calculations.

3.1.2. Band Gap

The space between the valence and conduction bands is referred to as the band gap, which is essentially the lowest amount of energy required to excite an electron so that it can participate in conduction. This energy is measured in electron volts (eV). If a gap exists between the high-energy conduction band and the low-energy valence band, then energy must be added to free the electrons. The valence band has a low energy level; if a gap exists between these two levels, then the valence band has a low energy level. The existence and magnitude of this band gap can be used to distinguish between conductors, semiconductors, and insulators.

The core molecule depicted in Figure 1 was transformed into a supercell by adding a multiple of 18 to explore the band structure of Mg. The resulting structure resembles that shown in Figure 3. In the following step, we used this structure to explore other quantum features of Mg. An alloy composed of Mg, Al, and Zn with this structure was also prepared. Prior to further analysis, this structure was subjected to geometrical optimisation.



Figure 3. Mg supercell for band structure calculations.

The band structure of Mg is depicted in Figure 4. No space can be found between the valence and conduction bands; therefore, the Mg metal is a conducting metal. The valence and conduction bands touch at location Q at an energy level of 8.85 eV and point F at -1.31 eV (Figure 5). This is the area where the Mg band gap value equals zero. Based on the graph, most electrons are possibly located at the Fermi level. This value is considered in the DOS analysis.



Figure 4. Band structure of the Mg slab using first-principle calculation.





The Mg band structure has the unusual quality of being well represented by the parabolic dependence of a free-electron gas [32]. From Figure 5, the energy gap for bands between 2.0 and -2.0 eV levels at point Q is 0.659 eV. However, no band gap (E = 0 eV) exists since Mg conducts electricity. The band gap value is quite similar to the theoretical value [33] and that of previous studies [32,34]. This means that the overlapping energy in both the conduction and valence band lies at >0 eV in those band structures [35], thus indicating the Fermi level of the structure, which is the highest energy level that the electron can occupy at absolute temperature. Some of the bands merge at point (Q, 8.85 eV). This might be the energy level of the overlapping conduction and valence bands.

In applications related to energy, the conductive property of Mg is critical for facilitating electron transmission. The following equation was adopted to determine the correlation between curvature and electron mobility. Equation (1) is the energy equation applied to the band structure and is expressed as:

$$E = \frac{h^2 k^2}{2m_e^*},\tag{1}$$

where *h* is the reduced Planck constant, *k* is the wave vector, and m_e^* is the effective electron mass. We can find the relation between the effective mass and energy curvature in an *E*–*k* diagram. The curvature denoted by the equation as follows:

$$curvature = \frac{d^2 E}{dk^2}.$$
(2)

Thus, the effective mass is denoted as follows:

$$m_e^* = \frac{h^2}{\frac{d^2 E}{dk^2}} \tag{3}$$

The effective mass is inversely proportional to the curvature of the energy band structure (Equation (4)). A high curvature leads to a low effective electron mass, resulting in high electron mobility. Thus, referring to Figure 5, the current flow and current density in the circuit could increase.

$$m_e^* \propto \frac{1}{\frac{d^2 E}{dt^2}} \tag{4}$$

Based on Equations (3) and (4), the curvature value is relatively high. As a result, the plate of Mg has a relatively low effective mass and high electron mobility because it is in the solid phase, where Mg atoms are densely packed with one another, leading to a high electron density and proof of high conductivity of Mg behaviour. If the molecular atoms are eroded from the plate and dissolved into the water, the electrons can travel as freely as possible.

3.1.3. DOS

To study the DOS of the Mg slab, we prepared a pure Mg slab and an alloy Mg slab introduced with two atoms of Al and one atom of Zn. Three positions of Al and Zn were chosen to analyse the effect of alloy position in the Mg slab. Figure 6 shows the differences in the position of the Mg and Mg alloys. Substitutional alloys were chosen because the corrosive effect of Mg is that the metal has a greater tendency to release electrons. Therefore, alloys for Mg must be substitutional. The corrosion mechanism of Mg forming metal ions will occur on the surface. So, the magnesium surface is more electropositive to forming metal ions. Therefore, the alloy was placed at three different depths to see the effect of corrosion on Mg.

Figure 7 shows the DOS data for all four Mg positions and Al and Zn alloys. No remarkable difference can be observed in the DOS distribution in each energy level. At the energy level of -7 eV, the DOS of Mg-Al-Zn alloy is higher than that of Mg alone. Additionally, the Mg-Al-Zn alloys with three different positions have a high DOS at energy levels from -2 to 3 eV around the Fermi level. This finding is in line with the hypothesis that alloying Mg with Al and Zn will increase the conductivity and electron density [35,36].



Figure 6. Pure Mg and Mg alloy Mg-Al-Zn with different positions: (**a**) Mg, (**b**) Mg-Al-Zn, (**c**) Mg-Al-Zn*, and (**d**) Mg-Al-Zn**.



Figure 7. The density of states of Mg, Mg-Al-Zn, Mg-Al-Zn*, and Mg-Al-Zn**.

To determine the contribution of individual atoms in this structure, the partial DOS data for all four Mg and Mg-Al-Zn (Figure 8) were plotted. The black, red, and blue colours represent PDOS of s-, p-, and d-orbitals, respectively. Since the PDOS graph in the s-orbital shows nearly similar behaviour for all four molecules, the d-orbital states were detected in most structures at the range of -6 to -9 eV with a PDOS value of almost 20 electrons/eV, except for Mg. This is due to the presence of Zn atoms. A previous study [20] showed similar results for the d-orbital PDOS value in Mg-Zn and Mg-Al structures. However, the differences may be seen in the p-orbital graph. This is because of the different position of Al

and Zn. In this figure, Mg exhibits the highest p-orbital peak around 0 eV. Some prominent peaks were observed in the range of 0.5–1.5 eV in Mg-Al-Zn, Mg-Al-Zn*, and Mg-Al-Zn**. The highest p-orbital peak in Mg-Al-Zn** lies in the energy range of -0.5 to -1.0 eV.



Figure 8. The partial density of states of (a) Mg, (b) Mg-Al-Zn, (c) Mg-Al-Zn*, and (d) Mg-Al-Zn**.

The potential permitted energy for transitions, such as thermal excitation, can be displayed using a DOS plot. An electron in a valence band is known as an occupied band. It has a Fermi energy of 0 eV and can absorb energy and momentum and move into a conduction band. In the conduction band, the energy difference between the final and initial states equals the absorbed energy. The likelihood of this phenomenon is proportional to the DOS at the initial and energies; this condition is proper regardless of the energy level being considered.

3.2. HOMO–LUMO Analysis

Knowledge of HOMO and LUMO, characteristics, and energies of molecules is essential in measuring their chemical reactivity. LUMO is responsible for the acceptance of electrons during molecular interactions, and its energy corresponds to the electron affinity (EA). HOMO is responsible for donating electrons, and its energy is associated with the ionisation potential (IP). The HOMO–LUMO energy gap explains the ending charge transfer interaction that occurs within the molecule and helps determine the electrical transport capabilities of molecules.

A molecule with a high frontier orbital gap (HOMO–LUMO energy gap) has poor chemical reactivity and high kinetic stability. Adding an electron to the high-lying LUMO to remove electrons from the low-lying HOMO is energetically unfavourable because the only method to remove electrons from the HOMO level, which is located below, is to add an electron to the LUMO level, which is located above. For instance, compounds with a large HOMO–LUMO energy gap tend to be stable and thus exhibit better chemical rigidity than compounds with a small HOMO–LUMO energy gap. When a HOMO–LUMO energy gap is large, the HOMO and LUMO energy levels become further apart. As shown in Table 1 Mg-Al-Zn* has a high HOMO–LUMO gap. Therefore, the Mg-Al-Zn* alloy with Al and Zn atoms positioned in the middle of the slab is highly stable and potentially has poor chemical reactivity. Therefore, the Al-Zn offers the advantage to Mg that Mg corrosion will be reduced due to the low reactivity. This phenomenon occurs because Mg has a



or oxidation.

natural propensity for reactivity, in the same manner as its natural propensity for corrosion

Table 1. Results of HOMO and LUMO energy with different Mg and alloys.

Nevertheless, this advantage will not be beneficial in solving the corrosion problems when the Al and Zn atoms at the surface are positioned either on top or at the bottom. Mg, which corrodes quickly, will cause the Al and Zn alloys to easily corrode when placed on the surface of the Mg slab higher up or lower down, as in positions 5(c) and (d). Additionally, the atoms of Al and Zn are more significant than those of Mg, making their bonds strong. Al-Zn alloying also offers the advantage to Mg that Mg corrosion will be reduced due to the low reactivity. This phenomenon occurs because Mg has a natural propensity for reactivity, in the same manner as its natural propensity for corrosion or oxidation.

One of the most successful explanations for the chemical stability of a molecule is the frontier molecule orbital theory, which considers HOMO and LUMO states. The HOMO and LUMO energies of the ligands and complexes yield information on energy's energetic behaviour and distribution [37]. The degree to which E_{HOMO} and E_{LUMO} have a negative magnitude determines the stability level of the compounds. The energy gap, also known as $E_{HOMO}-E_{LUMO}$, is a molecule's chemical reactivity and kinetic stability. A molecule with a wide HOMO–LUMO gap is considered to be a complex molecule because it is small and has significantly less polarisation [38]. The HOMO–LUMO gap in soft systems is modest, yet the gap size is wide and highly polarisable. A small HOMO–LUMO gap is related to anti-aromaticity, and a wide HOMO–LUMO gap is associated with high molecular stability, aromaticity, and low reactivity in chemical processes [39,40]. The HOMO energy denotes the ability to donate an electron, and the ability to acquire an electron is denoted by the LUMO energy. When the HOMO energy is high, the molecules become highly reactive with electrophiles. When the LUMO energy is low, the molecules become highly reactive with nucleophiles.

The DFT approach clarifies fundamentally significant and generally applicable ideas regarding the stability and reactivity of molecular structures. The energies of the FMOs, HOMOs, and LUMOs, which are helpful in quantum chemical calculations, have been used to gather information regarding chemical potential (μ), electrophilicity index (ω), electronegativity (χ), and softness (s), as well as hardness (η), to deduce the relations between energy, structure, and reactivity characteristics of complexes. The global reactivity can also be described from the data value of HOMO–LUMO using Koopman's theorem in the following Equations (5)–(11).

The chemical potential:

$$\mu = -\frac{(IP + EA)}{2} \tag{5}$$

where IP is equal to $-E_{HOMO}$ and EA is equal to $-E_{LUMO}$.

The hardness:

$$\mathfrak{n} = \frac{(IP - EA)}{2} \tag{6}$$

The softness:

$$\frac{1}{2n}$$
 (7)

The electronegativity:

$$\mathcal{X} = \frac{(IP + EA)}{2} \tag{8}$$

Global electrophilicity index:

$$=\frac{\mu^2}{2\mathfrak{n}}\tag{9}$$

Table 2 shows the global reactivity parameter value obtained from the HOMO and LUMO values in Table 1. These parameters are calculated using Equations (7)–(11). The data shown in this table reveal that there is not a huge discrepancy between the chemical potential value of Mg and that of Mg combined with Al and Zn. The chemical potential of Mg-Al-Zn** is 2.78 (eV), which is a higher value than that of Mg (2.74 eV), Mg-Al-Zn* (eV), and Mg-Al-Zn (2.63 eV). This pattern is also nearly identical to the values of hardness and electronegativity.

S =

ω

Table 2. Global reactivity properties of Mg and Mg-Al-Zn.

Global Reactivity	Mg	Mg-Al-Zn	Mg-Al-Zn*	Mg-Al-Zn**
Chemical potential (μ) , (eV)	2.74	2.63	2.71	2.78
Hardness (η) , (eV)	-0.15	-0.14	-0.21	-0.15
Softness (s), (eV^{-1})	-3.24	-3.48	-2.39	-3.45
Electronegativity (χ), (eV)	-2.74	-2.63	-2.71	-2.78
Electrophilicity index (ω), (eV)	-24.34	-24.05	-17.51	-26.63

Both electronegativity and hardness are useful properties because of their ability to assist in the prediction of chemical behaviour. There is a correlation between the value of hardness for different systems and the chemical hardness and softness that are defined empirically. The density functional formalism is where the theoretical foundation for the new quantities can be found. In light of the fact that molecular orbital (MO) theory is by far the most popular among chemists, it is essential to situate electronegativity and harness it within an MO framework. It has already been demonstrated that the MO theory of the chemical bond comprises the values of electronegativity and hardness for the bonding pieces.

3.3. Corrosion Analysis

Although Mg–air cells have relatively high voltage and energy density, there are still some scientific problems that limit their wide application. Some of the major issues affecting the performance of Mg–air cells include the release product of Mg (OH)₂, which attaches to the anode surface, and the self-corrosion that occurs on the Mg anode [41]. The physical and chemical reaction that occurs when metallic Mg is exposed to a particular environment can describe the corrosion mechanism. Song and Atrens [41] discussed several vital points that determine the type of corrosion in Mg alloys, such as self-discharge corrosion, galvanic corrosion, and localised corrosion.

In energy applications, Mg is usually used as a fuel to produce electrons. Mg corrosion that naturally occurs in the presence of water as an electrolyte is fully presented

in Equation (12). In an air–Mg fuel cell system, the cathode consisting of electrodes will contain a catalyst to balance the active oxidation reaction at the anode. The low oxygen reduction reaction at the cathode will produce hydroxide ions, as shown in Equation (13). The overall reaction of the anode and cathode is present as in Equation (14), and Equation (15) is the equation for Mg (OH)₂ precipitation in the electrolyte after corrosion.

$$Mg \rightarrow Mg^{2+} + 2e^{-} (anodic)$$
(10)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (cathodic)}$$
 (11)

$$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2 \text{ (overall)}$$
(12)

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$
 (deposition) (13)

Self-discharge corrosion (Equation (1)) is a side effect which promotes the hydrogen evolution reaction (HER) in Equation (2) and is a critical corrosion factor [42]. This phenomenon leads to a low Coulomb efficiency due to the negative differential effect (NDE) of Mg, which results in greater dissolution of Mg during the release process than expected from the current use [43]. Generally, corrosion is either an anodic or cathodic process. For most metals, such as iron, Zn, or steel, as the potential use increases, the anodic current increases in the anode, with a simultaneous decrease in the cathode current in the anode. Conversely, Mg exhibits unusual behaviours. The anodic and cathodic reactions of Mg anodes increase with increasing potential. This unique performance of Mg is called the NDE, which increases HER and thus accelerates the corrosion of the Mg anode [44]. Microgalvanic corrosion occurs due to the inconsistent anodic and cathodic reactions throughout the surface of Mg alloy because of its inhomogeneous composition, microstructure, and crystal orientation, which leads to the formation of galvanic couples or, in other words, act as micro-cathodes within the said alloy. One factor contributing to the micro-galvanic effect is grain boundary and orientation, where different grain sizes and textures exert different influences on the alloy's electrochemical performance and corrosion behaviour. Song [40] states that the corrosion rate of metal, to some extent, is correlated with its surface energy, which is somewhat associated with the atomic density of a given crystal plane.

Studies on the kinetics reaction and activation energy were performed on Mg molecules in the presence of water to analyse Mg corrosion. Normally, Mg will rust easily in the presence of NaCl. However, Mg also undergoes a rusting process in the presence of water. Therefore, this study focused on water only in the corrosion process. Other studies have used only water in the analysis of Mg properties, as shown by Nezafati et al. [19]. The diagram below shows the arrangement of the molecules. We also analysed Mg alloys with Al and Zn, whose positions can be discerned from the figure below. The initial hypothesis indicates that the Mg alloy can reduce the effect of Mg corrosion that is too active, apart from controlling Mg corrosion.

The transition state results for each Mg alloy position are listed in Table 3, where the reactant and product positions were grouped in the same way. Compared with alloyed Mg, pure Mg is located far from the water molecules, as evidenced by the higher activation energy compared with that of Mg alloy.

In a natural process, magnesium will react with water to generate magnesium hydroxide, represented by Equations (12)–(15). As shown in Equation (13), the oxygen molecule will be freed up (there will be no bond), and then OH^- will form a bond with the magnesium ion. The simulation carried out using this software results in the production of the transition state when the oxygen bond is broken, and the process of the formation of Mg(OH)₂ is described by Equation (15). As a result, the distance between oxygen, magnesium, and other elements is large and considered no bonding. In theory, there is a very slight reaction that takes place between magnesium and cold water. After a period of time, hydrogen bubbles begin forming on the magnesium surface, and the coil of magnesium ribbon will typically rise to the top of the mixture. The magnesium hydroxide that was generated is almost completely insoluble in water, and it creates a barrier on the magnesium, which prevents any further reaction from occurring. However, the reaction soon comes to an end. A reaction between a metal and cold water will result in the production of metal hydroxide as a product of the reaction. Steam catalyses the formation of the metal oxide in this reaction [45]. This is due to the fact that the metal hydroxides undergo thermal decomposition, in which they split up into oxide and water upon heating.



Table 3. Results of molecule arrangement for reactant, product, and transition state after geometry optimisation.

According to Table 4, the compound with the lowest activation energy is Mg-Al-Zn, followed by Mg. Although the Mg-Al-Zn* system has the highest activation energy, the Al and Zn atoms are located on the surface of the Mg slab, which is able to prevent the corrosion of the Mg. Activation energy is the energy that must be present for Mg to corrode. This finding suggests that Mg-Al-Zn is the most susceptible to corrosion. If the Al-Zn alloy is embedded in the middle of the Mg slab, then the corrosion of Mg might be inhibited. This result is in line with a previous finding, that is, the Al and Zn atoms grouped in the middle can assist in the stable and secure binding of Mg atoms. A high activation energy value also indicates that corrosion occurs slowly in the presence of water compared to diluting in salt water or at temperature. This is in line with the results from Zhao et al., who compared several activation energy values in the range of 0.2–6 eV [46]. The activation energy's additional alloying elements in Mg also can be studied using its surface energies. A study conducted by Nezafati et al. explained the corrosion effect of Mg added with Al, Zn, and Y, using the surface energy value in different surface planes shown in Table 5 [47].

Based on that, the surface energy values for the added alloying elements were lower than that for the plain Mg.

Table 4. Reactant energy, transition state, product energy, and activation energy for each Mg and Mg-Al-Zn component.

Component	Reactant Energy (eV)	Transition State Energy (eV)	Product Energy (eV)	Activation Energy (eV)	Activation Energy (KJ/mol)
Mg	200,040.65	200,047.91	200,045.41	2.50	241.20
Mg-Al-Zn	245,335.26	245,342.53	245,340.71	1.82	175.60
Mg-Al-Zn*	245,320.15	245,326.91	245,322.68	4.23	416.84
Mg-Al-Zn**	245,334.90	245,343.47	245,340.09	3.38	326.12

Table 5. Calculated surface energies (kJ/mol) of Mg systems with different surface planes and alloying elements [47].

Surface Planes	Components	Surface Energies (KJ/mol) [42]	Components	Activation Energy (KJ/mol)
Basal (0001)	Mg	33.02	None	241.20
	Mg-Al	31.07	Mg-Al-Zn	175.60
	Mg-Zn	31.46	Mg-Al-Zn*	416.84
	Mg-Y	31.51	Mg-Al-Zn**	326.12

Alloying Mg will help prevent its corrosion, but the position of the alloy atoms must be carefully considered to ensure that the additional alloy atoms will help reduce corrosion. Modelling studies, such as the current one, are helpful in assessing the characteristics of materials before their actual production.

4. Conclusions

This study analysed the molecular properties of Mg and the difference in its properties when combined with Al and Zn. The molecular properties of Mg are important in improving its function for wide application, especially in drug delivery and energy. Investigation of Mg's band structure discovered the lack of a band gap, indicating that this element conducts electricity. Additionally, the Fermi level is at 8.85 eV. Curvature examination revealed that Mg possesses strong electron mobility and high curvature. DOS analysis showed that the DOS shifts in the presence of alloy atoms, including Al and Zn. Specifically, the electron density increases to -7.5 eV compared with that in pure Mg. HOMO and LUMO analysis indicated a relatively large HOMO–LUMO gap in Mg-Al-Zn*, suggesting its low chemical reactivity and high stability. Corrosion experiments showed that Mg-Al-Zn has a larger activation energy than other metal combinations. Therefore, this material is less likely to corrode than other alloys.

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