Crystal structures of a Mg–Zn–Y alloy: A first-principles study

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Abstract

We use first-principles density functional theory total energy calculations based on pseudopotential and plane-wave basis to examine the energetics of the periodic structures with different stacking sequences in Mg–Zn–Y alloys. For pure Mg, we find that the 6-layer structure with the ABACAB stacking is the second most stable (among the 2-, 3-, 4- and 6-layer structures considered), after the lowest energy hcp structure with ABAB stacking. The addition of 2% Zn leads to stabilization of the structure to 6-layer sequence. The stacking fault energies in the 4- and 6-layer structures were found to be significantly higher than that in the 2-layer structure. Charge density analysis shows directional bonding and accumulation of charges in the basal plane of 4- and 6-layer structures.

Keywords: DFT calculation; Stacking fault energy; Magnesium; Mg–Zn–Y

1. Introduction

Non-equilibrium processing (such as rapid quenching) of multi-component alloys can give rise to refined microstructures as well as phases with novel crystal structures, which in turn give rise to unique combinations of mechanical properties [1–4]. The alloys of Mg are special in the sense that a variety of interesting phases that are crystalline, quasicrystalline, nanocrystalline and amorphous in nature can be obtained depending on the processing conditions used. Since Mg-based alloys are attractive for many engineering structural applications owing to their low density and high specific strength, it is important to understand the evolution of these structures and the factors governing their mechanical properties.

Recent studies show a long periodic hexagonal 6-layer structure in an alloy of composition Mg97Zn1Y2 (at.%) that was processed by employing rapid solidification technique [2]. Similarly, a 14-layer sequence was observed in melt spun Mg97Ln2Zn1 (Ln = lanthanide metal) alloys with atomic scale enrichment of Ln and Zn elements into misfit atomic array sites [3]. A 14- to 6-layer transition was reported in alloys that contain Y or Sm or Gd. All these alloys were observed to exhibit good combination of strength, ductility and toughness. In another report, the addition of Zn was found to improve the creep strength of Mg–Y solid solution alloys at temperatures 550–650 K [4]. It was proposed that Zn suppresses the non-basal slip that is predominant at such temperatures through the formation of planar defects and confinement of dislocations due to a decrease in stacking fault energy in the basal plane [4]. The present work uses ab initio calculations to determine the energetics of various layered structures and stacking faults in order to rationalize the aforementioned experimental observations.

2. Computational details

Total energy calculations were performed by employing a local density approximation of the density functional theory and using Troullier–Martins pseudopotentials with
ABINIT [5] package. A plane wave basis with an energy cut-off of 24 Ry (increased to 60 Ry in case of Zn) was used to represent Kohn–Sham wave functions. Crystal structures were optimized by using the Hellman–Feynman forces and stresses. The relaxed γ surface on (0001) slip plane is constructed in Mg 2-layer (hcp), 4-layer (d-hcp), and 6-layer structures by calculating the total energies of supercells that contains 12, 8, and 6 atomic layers, respectively. One atom in each layer forms the basis of the supercell. Charge density analysis is carried out by the post-processing of the output density files as obtained by ABINIT. Further analysis of the charge densities involves the use of “Atoms In Molecules” AIM utility of ABINIT to obtain the critical points. An attempt was made to correlate the results obtained by total energy calculation, stacking fault energy calculation and charge density analysis.

3. Results

First, lattice constants and bulk moduli of Mg, Zn, and Y were obtained in order to test the pseudopotentials and calculation parameters through comparison with experiment. Results show that predicted values are within acceptable theoretical errors as shown in Table 1. The differences between calculated and experimental values, especially in the case of Zn, are due to the following two factors: (a) the calculations were performed on single crystals, whereas the experimental data is generated on polycrystals; and (b) anisotropy in the elastic modulus of single crystals.

Total energy optimizations were conducted for the different stacking structures of pure Mg. The total equilibrium energy ranking, in the ascending order, was found to be 2-layer (hcp), 6-layer, 4-layer (d-hcp) and 3-layer (fcc) as shown in Fig. 1. For Mg(2 + 1) (2 + 1)2) Mg3L(FCC) Mg4L(d-HCP) Mg6L

Fig. 1. Results of the total energy calculation of different layered structures of Mg.

Further, calculations were carried out constructing a supercell containing 12 atoms in order to find the generalized stacking fault (GSF) energy surface for pure Mg. This is because the relationship between electronic structure and mechanical properties of materials is determined by the interfacial energetics under different modes of displacement to applied stress; the stability of stacking faults on the slip planes of a crystal is intimately connected with the nucleation of dislocations on these planes. Energy release rate needed for dislocation nucleation is proportional to the unstable stacking fault energy, γus, which corresponds to the lowest energy barrier encountered in sliding one half of a crystal relative to another along a slip plane [6]. The change in energy per unit area of the crystal as a function of displacement vector Q, varied on the slip plane to scan a unit cell is called the generalized stacking fault energy surface or γ surface. Generalized stacking fault energy is a fundamental material property that can be obtained by first principles calculations [7].

Slip on (0001) plane of hcp was considered. The results are shown in Fig. 2 for 2-layer, 4-layer and 6-layer structures. The calculated value of unstable stacking fault energy was found to be 107 mJ/m² for 2-layer. This value

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Lattice parameters (Å)</th>
<th>Bulk Modulus (GPa)</th>
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<tr>
<td></td>
<td>Calculated</td>
<td>Experimental</td>
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<tr>
<td>Mg2L(AB)</td>
<td>a = 3.1643</td>
<td>a = 3.2094</td>
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<td></td>
<td>c = 5.0246</td>
<td>c = 5.2108</td>
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<td></td>
<td>e/a = 1.588</td>
<td>e/a = 1.623</td>
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<td>Zn(AB)</td>
<td>a = 2.5711</td>
<td>a = 2.6649</td>
</tr>
<tr>
<td></td>
<td>c = 4.8252</td>
<td>c = 4.9463</td>
</tr>
<tr>
<td></td>
<td>e/a = 1.876</td>
<td>e/a = 1.856</td>
</tr>
<tr>
<td>Y(AB)</td>
<td>a = 3.6458</td>
<td>a = 3.6474</td>
</tr>
<tr>
<td></td>
<td>c = 5.66</td>
<td>c = 5.7306</td>
</tr>
<tr>
<td></td>
<td>e/a = 1.552</td>
<td>e/a = 1.571</td>
</tr>
</tbody>
</table>
agrees well with the experimental value (60–150 mJ/m²) and that obtained by other theoretical calculations [8].

GSF calculations are extended to 4-layer and 6-layer structures and the results are summarized in Fig. 2. A local minimum along the (110) direction indicates the intrinsic stacking fault energy value, \( \gamma_s \) [6]. It is found that the stacking fault energy values are higher in case of 4-layer (529 mJ/m²) and 6-layer (469 mJ/m²) structures.

The mechanical behaviour of metals is closely related with the various attributes of the metallic bond, most implicitly bond directionality [9,10]. The topological property of charge density illuminates this issue [11]. Bader analysis or atom-in-molecule (AIM) analysis uses the scalar field charge density as input and through critical point analysis (zeros of the gradients of this field) relates its topology to the bonding in the molecular and solid state structures. Recent studies address an association of the stacking fault energy with redistribution and topological properties of the charge density [10,12].

Charge densities are plotted in Fig. 3 (a–c) for 2-layer, 4-layer and 6-layer structures of Mg, respectively, at the isovalue of 99% of the maximum value for charge density.

There is no lobe for 4-layer structure at the basal plane which is observed in case of 2-layer and 6-layer structures. Critical point analysis results by AIM are shown in Fig. 4 (a–c) for 2-, 4- and 6-layer structures, respectively. While the cage critical points for the 2- and 6-layer structures are within the tetrahedral voids of the lattice, they are seen to be displaced towards the basal plane in the 4-layer structure as shown Fig. 4(b).

### 4. Discussion

The total energy calculations reveal that 6-layer stacking is energetically more favourable vis-à-vis 3- and 4-layer structures. On the other hand, energy of the 6-layer structure with 2% of Zn is comparable with the energy of 2-layer structure with 2% of Zn. These results clearly indicate that addition of Zn stabilizes the 6-layer structure further, thus confirming the experimentally observed structure of Mg₉₇Zn₁Y₂ alloy by Inoue et al. [2]. Stacking fault energy calculations show higher values for 4-layer and 6-layer structures as compared to the 2-layer structure. High value of stacking fault energy reduces the distance between
partial dislocations separated by a faulted region. This increases the density of stacking faults per unit area of the crystal which is also observed by Inoue et al. [2] in HRTEM image. Charge density plots show higher value of charge density at the edges of the unit cell surrounding the B and C atoms in all the three structures. Another lobe of charge density appears at the basal plane for 2-layer and 6-layer at the point of projection of B atom but this signature is absent in case of 4-layer structure. The inhomogeneous nature of the charge indicates the bond directionality in all the three structures. Critical point analysis demonstrates the appearance of cage critical points (CCPs) within the tetrahedral void of 2-layer and 6-layer structures which is a signature of the close packed metal [9]. The cause for anomalous behaviour of 4-layer structure is not yet fully understood.

5. Summary

First-principles total energy calculations were performed employing density functional theory to understand the energetics of various layered structures of Mg in order to address the unresolved issues of the unique structure and mechanical properties of Mg97Zn1Y2 alloy observed by Inoue et al. [2]. It was found by calculation that the 6-layer structure is the next stable structure to the lowest energy 2-layer structure. Addition of 2% of Zn stabilizes the 6-layer structure additionally as the energy is comparable with the 2-layer structure doped with 2% of Zn. Stacking fault energy calculations reveal higher values in case of Mg 4-layer and 6-layer structures indicating high density of stacking faults per unit area of the 4-layer and 6-layer structures. Charge density calculation results also show
anomaly in case of 4-layer structure that is yet to understand fully.

References


Fig. 4. Critical point plot obtained by the AIM analysis for (a) 2-, (b) 4- and (c) 6-layer structures.