Correlation between bonding, vacancy migration mechanisms, and creep in model binary and ternary hcp-Mg solid solutions

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ABSTRACT
High temperature creep deformation of hcp-Mg alloys is dominated by dislocation climb driven by out-of-plane (OOP) vacancy migration. Past experiments and atomistic simulations have indicated that Zn addition reduces vacancy migration tendencies and improves creep resistance. Here, we have compared in-plane (IP) and out-of-plane (OOP) vacancy migration mechanisms in binary Mg–X (Ca, Y, and Gd) and ternary Mg–X (Ca, Y, and Gd)–Zn alloys using density functional theory based first principles computations. Irrespective of Zn addition, the migration barrier for OOP diffusion was consistently higher than IP in our prototype binary and ternary alloys. The presence of Zn in ternary systems, however, substantially increases the OOP activation barrier relative to binary alloys. The higher OOP barrier in Mg–X–Zn was attributed to favorable local relaxation, enhanced charge localization, higher interplanar bond stiffness, and greater s orbital electron occupancy in the peak saddle state. Combined, these factors restrict non-conservative dislocation climb by impeding out-of-plane vacancy movement and improve the creep resistance of ternary Mg–X (Ca, Y, and Gd)–Zn alloys.

I. INTRODUCTION
The past decade has seen considerable interest1–4 in magnesium (Mg)-based alloys because of their low density, relatively low processing temperature, and high specific heat, which are promising for powertrains, engine blocks, and other automotive applications.5 Despite such a large body of work, a limited number of commercial Mg alloys are available for engineering applications because of their poor creep resistance, inadequate yield strength, low formability, and other limitations.6,7

Here, we have examined some vacancy mechanisms contributing to creep deformation of Mg alloys. Creep is a time dependent and stress-temperature sensitive inelastic deformation occurring via various mechanisms in solids.8–10 When both temperature and stress are high and strain rate has a power law dependence on stress, creep is contributed by dislocation creep involving various mechanisms such as non-conservative vacancy-assisted dislocation climb over obstacles, thermally activated cross-slip, solute induced viscous drag on dislocations, movement through dislocation intersection, and grain boundary sliding. On the contrary, at elevated temperature,10 \( T \approx T_M \) (\( T_M \) is the melting point in thermodynamics temperature) and when strain rate has a linear dependence on stress, non-dislocation based diffusional creep known as the Nabarro–Herring creep occurs in fine grain polycrystalline materials via vacancy diffusion through grains. Grain boundaries act as perfect sources and sinks for vacancies. Thus, grains get elongated without dislocation slip or climb. Consequently, Coble creep occurs at relatively lower temperatures \((T < 0.5 T_M)\) where the contribution of grain boundary diffusion is larger than that of self-diffusion through grains and thus diffusion of vacancies along grain boundaries controls creep. In the case of pipe diffusion, atomic transport occurs through dislocation cores. The segregation effects of solutes used in this study, and their consequent effect on diffusion and dislocation climb, are considered in Sec. III. Furthermore, typical
operational temperatures for Mg–alloy parts range between 450 and 520 K, i.e., 0.68 – 0.87\(T_d\) where lattice diffusion becomes more important.

Precipitation hardening, one of the prominent strengthening mechanisms in Mg alloys,\(^{11} \) has been shown to improve their creep resistance. For example, several studies\(^ {12,15} \) have shown that precipitates embedded in hcp-Mg matrix of Mg-rare earth (RE) alloys retard dislocation motion and resist creep deformation, which impart high temperature strength to such alloys. Recently, it was demonstrated that a minor quantity of Zn addition to Mg–Nd–La alloys substantially increases their creep resistance by facilitating the formation of basal precipitate phases, and, to some extent, segregation of Zn atoms at defects.\(^ {20} \) Depending upon the Mg–alloy system, its microstructure, and applied stress and temperature regimes, the creep deformation is controlled mainly by either dislocation climb or viscous glide of dislocations under solute drag. Vagarali and Langdon\(^ {15} \) have reported the transition from solute cross-slip in Mg; it was reported that Zn is more effective in hindering activated dislocation processes occur.\(^ {12,15} \) The solute–vacancy binding energy will strongly attach to the vacancy and prevent cross-slip is an important step in creep resistance.\(^ {13} \) Therefore, our focus on the vacancy mechanism as the unit process driving creep is valid.

Understanding the role of precipitates and their modification to prevent cross-slip is an important step in creep resistance.\(^ {13} \) Since cross-slip is related to stacking fault energy (SFE), solutes that decrease SFE tend to increase the creep resistance by decreasing the cross-slip. Suzuki et al.\(^22 \) have studied the high temperature creep response of Mg–Y and Mg–Y–Zn alloys at 550 K and 650 K. They have found that the Zn addition leads to the formation of planar defects spreading on the basal plane of the Mg matrix, which act as obstacles to non-basal slip of dislocations. They also reported the reduction in SFE and thereby confinement of dislocations in the basal plane and suppression of non-basal slip. Recently, it was reported that Zn is more effective in hindering activated cross-slip in Mg–Nd–Zn alloys.\(^ {23} \) Thus, non-basal dislocations are not expected to play a significant role in the creep of these alloys and are ignored in this study.

Solute diffusion kinetics and thermodynamics indicate the formation of precipitates and understanding solute–vacancy binding provides help in the quantitative picture of diffusion.\(^ {24-27} \) The relative binding energy between solute and vacancy determines which atomic clustering process is dominant and which precipitate nucleation processes occur.\(^ {27} \) The solute–vacancy binding characterizes the microalloying additions in Mg, because such additions alter the atomic clustering processes occurring prior to nucleation of precipitates and modify the morphology of precipitates.\(^ {27} \) Therefore, it is important to understand the binding energies between the solute and the vacancy in Mg alloys.

Despite the valuable perceptions given by binding energy values for solute diffusion in Mg, vacancy-mediated dislocation climb is the primary mechanism driving high temperature creep deformation of Mg alloys.\(^ {15} \) Therefore, solutes with favorable vacancy binding energy will strongly attach to the vacancy and restrict long range diffusion toward dislocation cores and hinder dislocation climb. Recently,\(^ {23} \) it was shown that such hindrance to non-conservative dislocation motion likely occurs in Mg–Nd–Zn alloys due to the formation of stiffer directional bonds or covalent bonds within the Mg–alloy matrix and dramatically improves their creep strength.

Here, we explore whether ternary Zn addition to binary Mg–X (Ca, Y, and Gd) solid solutions can inhibit dislocation climb by examining vacancy diffusion pathways related to such non-conservative dislocation motion. Therefore, in the present investigation, we first calculate the solute–vacancy interaction binding energies and discuss their trends in terms of solute size. Next, we focus on Mg–vacancy-mediated diffusion mechanisms, e.g., within \((0002)_{\text{Mg}}\) basal (in-plane, IP) and between two basal planes (out-of-plane, OOP), by examining vacancy formation and migration energy barrier in binary Mg–X(Ca, Y, and Gd) and ternary Mg–X–Zn alloys. Finally, we establish whether stiffer directional bonds form in an Mg matrix near the solutes and if such bonds can improve the creep response of Mg alloys. The broader objective was to generalize the effect of Zn on Mg–X diffusion mechanisms on the basis of detailed energetic computations and chemical bonding characterization.

This paper is organized into three main sections (Secs. II– IV). Section II presents the simulation method and computational details, especially the theoretical basis for first principles calculations using the density functional theory (DFT). In Sec. III, we present the results for the solute–vacancy binding energy and its variation with solute size, vacancy formation energy, and migration energy barrier in binary Mg–X and ternary Mg–X–Zn alloy solid solutions. We discuss the energetics based on charge density distribution and electron density calculations. Section IV summarizes our results.

II. SIMULATION METHOD AND COMPUTATIONAL DETAILS

First principles calculations were performed using the Vienna ab initio Simulation Package (VASP) embedded in the MedeA Simulation environment.\(^ {28} \) A projected augmented plane wave (PAW) method was utilized, and generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)\(^ {29-30} \) parameterization was used to describe electron exchange and correlation. The Monkhorst–Pack scheme with \(10^{-7} \) eV threshold and a Methfessel-Paxton smearing width of 0.2 eV. The global energy convergence was achieved with 0.001 eV/atom.

Calculations were performed using 96 atom supercells and k-spacing of 0.1 Å\(^{-1}\). All calculations were performed at 0 K with a plane wave cutoff energy of 550 eV. Ground state structures were obtained by relaxing ionic positions, cell shape, and cell volume until Hellmann–Feynman forces on each atom were below 0.001 eV/Å.

Point defects were introduced by adding and/or removing appropriate atoms. Vacancy was created by removing one Mg atom from a hcp supercell. Ca, Y, and Gd were placed at the Mg lattice site, as a first nearest neighbor (NN) to the Mg atom. A Zn atom was also placed at the first nearest neighbor site to Ca, Y, and Gd atoms. First, we define the vacancy formation energy for a single vacancy (V) present in pure Mg as

\[
\Delta E_f^V = E(Mg_{6n-1} + V) - \frac{(n-1)}{n} \times E(Mg_{6n}).
\]

(1)
Equations (2) and (3) define dilute mixing energy for solute (X) in binary and ternary alloys.

**Binary Mg–X (Ca, Y, and Gd) alloy:**

\[ E_{\text{mix}}(X_3) = E(Mg_{n-1}X_3) - \left( \frac{n-1}{n} \right) E(Mg_{n}) - E_{\text{ref}}(X). \]  

**Ternary Mg–X (Ca, Y, and Gd)–Zn alloy:**

\[ E_{\text{mix}}(X_3Zn_2) = E(Mg_{n-2}X_2Zn_3) - \left( \frac{n-2}{n} \right) E(Mg_{n}) - E_{\text{ref}}(X) - E_{\text{ref}}(Zn). \]  

\[ E_{\text{ref}}(X) \text{ and } E_{\text{ref}}(Zn) \text{ are, respectively, the reference energy per atom of element } X \text{ and Zn in their ground state structures (refer to Table I).} \]

Subsequently, we computed solute–vacancy binding energy \([E_{\text{sv}}^2(V)]\) using Eqs. (4) and (5) as follows:

**Binary Mg–X (Ca, Y, and Gd) alloy:**

\[ E_{\text{sv}}^{(X)}(V) = E(Mg_{n-1} + V) + E(Mg_{n-1}X_3) - E(Mg_{n-2}X_3 + V) - (d-1)E(Mg_{n}). \]  

**Ternary Mg–X (Ca, Y, and Gd)–Zn alloy:**

\[ E_{\text{sv}}^{(X,Zn)}(V) = E(Mg_{n-1} + V) + E(Mg_{n-1}X_3) + E(Mg_{n-3}Zn_3) - E(Mg_{n-3}X_2Zn_3 + V) - (d-1)E(Mg_{n}). \]

Here, \( E(Mg_{n-1}X_3) \) is the total energy of a cell containing \( (n-1) \) Mg atoms, and a solute atom \( (X_3 = \text{Ca, Y, and Gd}) \). \( E(Mg_{n-1}Zn_3) \) is the total energy of a cell containing \( (n-1) \) Mg atoms, and a Zn atom. \( E(Mg_{n-2}X_2Zn_3) \) is the total energy of a cell containing \( (n-2) \) Mg atoms, solute atom \( (X_3 = \text{Ca, Y, and Gd}) \) and a Zn atom. \( E(Mg_{n-1} + V) \) is the total energy of a cell containing a vacancy. Number of Mg atoms \( n = 96 \). \( E(Mg_{n-2}X_3 + V) \) is the total energy of a cell containing \( (n-2) \) Mg atoms, solute atom \( (X_3 = \text{Ca, Y, and Gd}) \) and a vacancy. \( E(Mg_{n-3}X_2Zn_3 + V) \) is the total energy of a cell containing \( (n-3) \) Mg atoms, solute atom \( (X_3 = \text{Ca, Y, and Gd}) \), Zn atom, and a vacancy. "d" is the number of defects present in a system. Subscript "S" denotes a substitutional site. We use literature convention of positive binding energy \( E_{\text{sv}} < 0 \) where larger \( E_{\text{sv}} \) corresponds to stronger solute–vacancy binding.

To get a quantitative measure of how the atomic size of each solute impurity \( X \) influence binding, we also calculated the solute impurity volume, \( V_{\text{imp}}(X) \), defined as the volume difference induced by placing a single solute impurity into pure Mg.

\[ V_{\text{imp}}(X) = V(Mg_{n-1}X_3) - V(Mg_n). \]

In the presence of Zn, impurity volume, \( V_{\text{imp}}^{(Zn)}(X) \), is defined as

\[ V_{\text{imp}}^{(Zn)}(X) = V(Mg_{n-2}X_2Zn_3) - V(Mg_n). \]

where \( V(Mg_n) \), \( V(Mg_{n-1}X_3) \), and \( V(Mg_{n-2}X_2Zn_3) \) represent, respectively, volumes corresponding to ground state structures of pure Mg, Mg with solute impurity \( (X_3) \), and Mg with solute impurity \( (X_3) \) and Zn.

The nudged elastic band (NEB) method developed by Jónsson and co-workers has been applied to a broad category of metallurgical problems involving the determination of migration barriers for solute diffusion. In the present study, we have computed energy barrier for in-plane and out-of-plane vacancy migration using the NEB method. In NEB, an interpolated chain of configurations (images) between the initial and final states are connected by springs and relaxed collectively to yield a minimum energy pathway (MEP) of the vacancy going from its initial to final state. The highest energy image of MEP is considered here as a saddle image (transition state). The energy barrier is defined as the difference between the energies of the saddle and stable end point states of the diffusing system. In this study, all the images are relaxed until the maximum force acting on an atom is below 0.001 eV/Å.

Finally, we have analyzed these computed energy values in terms of charge density distributions using an iso-surface level of 0.015 e/Å³ to visualize bonding between the atoms. In the density of states calculations, we have evaluated and compared occupancy number of Mg atom in terms of s, p, and d orbitals. The electron occupation numbers are obtained by integrating partial density of states (PDOS) of the Mg atom up to Fermi energy.

### III. RESULTS AND DISCUSSION

We begin by examining solute–vacancy binding energies, which play an important role in understanding micro-alloying additions in Mg and discuss how it changes with solute size. Next, we focus on vacancy-mediated dislocation climb where we compare vacancy formation energy in binary Mg–X (Ca, Y, and Gd) and ternary Mg–X–Zn alloys. This helps us to understand and construct a reasonable initial and a final input configuration to determine the MEP for vacancy diffusion. Subsequently, vacancy migration and activation energies were computed and compared in these alloys. Finally, we rationalize the computed energy values of each system in terms of charge density, density of states, and to elucidate whether engineering stiffer directional bonds in Mg matrix can improve creep response of Mg–X and Mg–X–Zn alloys.

### A. Solute–vacancy binding energy in Mg alloys

Figure 1 schematically shows the first nearest neighbor (NN) out-of-plane (OOP) and in-plane (IP) vacancy placement sites, and the nominal migration trajectory (indicated by arrows in Fig. 1). Irrespective of the location of the vacancy within pure Mg hcp lattice, its formation energy \( \Delta E_i \) was 0.81 eV, which is consistent

### TABLE I. Calculated reference energies, \( E_{\text{ref}}(X) \) in eV/atom, for Ca, Y, Gd, and Zn atoms.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Y</th>
<th>Gd</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{ref}}(X) )</td>
<td>-1.93</td>
<td>-6.43</td>
<td>-4.58</td>
<td>-1.11</td>
</tr>
</tbody>
</table>
with literature reports. Figure 2(a) compares the solute–vacancy binding energies of binary and ternary Mg alloys and reveal that Zn addition increases binding energies. Specifically, the presence of Zn atom increases the solute–vacancy binding energy of Mg–Ca from 0.12 eV to 0.33 eV, Mg–Y from −0.01 eV to 0.19 eV, and Mg–Gd from 0.004 eV to 0.22 eV.

Figure 2(b) compares solute–vacancy binding energies as a function of solute volume, calculated by coupling a hard sphere model to our DFT geometries, where the Mg radius is defined as half of the Mg–Mg nearest neighbor (NN) distance while solute radii are obtained by subtracting the Mg radius from the solute–Mg NN distance (see Table II) (Ca is the largest solute atom among the elements considered in this work). Results indicate that larger solutes have higher binding energies with vacancies. This can be explained in terms of a simple strain model of Shin and Wolverton. Large solute atoms induce significant strain on the surrounding Mg lattice. However, neighboring vacancies allow the solute atoms to relax toward the vacancy and away from the neighboring Mg atoms. The comparison of binding energy values of Mg–Ca, Mg–Y, and Mg–Gd indicate that Ca strongly binds to its neighboring vacancy [Fig. 2(b)]. Therefore, a vacancy in Mg–Ca binary is constrained from participating in dislocation climb during creep deformation. Our results also predict Y to be repulsive with vacancies although it has significantly large volume as a dilute impurity in Mg. In general, for binary alloys considered in this work, the solute–vacancy binding energies have a trend of Mg–Ca > Mg–Gd > Mg–Y. Figure 2(b) also reveals that Zn has a positive solute–vacancy binding and a negative impurity volume. Since such volume was computed with respect to pure Mg lattice [see Eq. (6)], negative value indicates local “contraction” of regions around the smaller Zn atom. Notwithstanding, Zn solute maintains the same trend in binding energies as the binaries, i.e., Mg–Ca–Zn > Mg–Gd–Zn > Mg–Y–Zn [see Fig. 2(b)].

Figure 3 compares the vacancy formation energy in binary and ternary Mg alloys. There are several formalisms mentioned in the literature to calculate the formation energy of a vacancy near a solute in an alloy. However, in case of binary alloys, we calculated the vacancy formation energy near a solute by taking the difference of $\Delta E^V_{\text{conf}} - E_{\text{vac}}(X_S)$ [refer to Eqs. (1) and (2) and see Table III]. We calculated the vacancy formation energy for Mg–Ca and Mg–Y alloys as 0.81 eV and 0.88 eV, respectively, which is consistent with the literature. Therefore, on a similar basis, in the case of Mg–X (Ca, Y, and Gd)–Zn ternary alloys, we
used the energy difference of $\Delta E_V^X = E_{\text{vac}}(X_2Zn_0)$ [refer to Eqs. (1) and (3) and see Table III] to evaluate the vacancy formation energy near a solute. Note that Mg-X vacancy formation energies do not exhibit any discernable trend. However, in the presence of a Zn atom, for Mg–Y and Mg–Gd alloys, vacancy formation energy increases from 0.88 eV to 0.98 eV and 0.86 eV to 1.12 eV, respectively, while significant change was not observed for Mg–Ca–Zn. Zn addition also produces favorable mixing energies with the trend Mg–Gd–Zn > Mg–Y–Zn > Mg–Ca–Zn—that is similar to vacancy formation energy trend.

The apparent opposite trends in solute–vacancy binding and vacancy formation (and mixing) energies is rationalized using their appropriate formulas, e.g., comparing corresponding equations for $\Delta E_V^X$ and $E_{\text{mix}}(X_2Zn_0)\langle V \rangle$ in Sec. II. $\Delta E_V^X$ for vacancy formation computes the energy required to remove an Mg atom from the surrounding pristine lattice, while $E_{\text{mix}}(X_2Zn_0)\langle V \rangle$ is a measure of the “bonding strength” between the solute and vacancy. Thus, in the case of Mg–Ca–Zn, it is easier to create a new vacancy by removing an Mg atom (see Fig. 3). The resistance to vacancy formation is also highlighted by the more negative energy of mixing. However, once the vacancy is created, the larger Ca atom occupies the “extra” space due to local lattice relaxation, which leads to higher solute–vacancy binding energy (see Fig. 2). The opposite trend occurs in Mg–Gd–Zn.

The Zn-induced enhancement of solute–vacancy binding energies was analyzed qualitatively in terms of differences in charge density distribution ($\Delta \rho$). Figure 4 shows the excess $\Delta \rho$ along the c axis for OOP nearest neighbor (NN) vacancies in binary and ternary Mg–alloys as yellow colored contours of isocharge surfaces. In Fig. 4, each supercell had six basal planes and the isocharge surfaces appear to “penetrate” the basal planes next to the solutes. For Mg–X (Ca, Y, and Gd)–Zn alloys, the $\Delta \rho$ distribution between X (Ca, Y, and Gd) and Zn atom is larger than that between the solute and a Mg-2 atom in binary Mg–X (Ca, Y, and Gd) alloys. The enhanced $\Delta \rho$ distribution can be viewed by comparing the spatial extent of isocharge surfaces in Mg–X–Zn (top row in Fig. 4) and Mg–X (bottom row in Fig. 4). Qualitatively, we find that isocharge surfaces extend end-end-in case of ternary Mg–X–Zn but falls shorter in binary Mg–X.

Such elevated $\Delta \rho$ indicates stronger and stiffer bonds between Zn and solutes (Ca, Y, and Gd).24,25 This enhancement in bond strength is reflected in shorter bond lengths. For example, in Fig. 4, the Mg (–2)–Ca bond length is 3.2 Å in the binary Mg–Ca alloy, but the addition of Zn (by replacing Mg-2 atom) reduces this distance to 3.1 Å. Similarly, for binary Mg–Y and Mg–Gd alloys, the Mg (–2)–Y and Mg (–2)–Gd bond lengths are reduced from 3.2 Å to 3.0 Å when an Mg-2 atom is replaced by a Zn solute. This localization of charge density points to an increased local directional bonding or bonds with greater degree of covalent character.24,43 Similarly, the bond length between an alloying atom and Mg-1 atom marginally decreases in the presence of a Zn atom when compared to corresponding bond lengths in binary systems. For example, in the presence of Zn atom, the Mg (–1)–Ca bond length reduces from 3.39 Å to 3.36 Å. For Mg–Gd and Mg–Gd–Zn, it reduces from 3.24 Å to 3.21 Å and 3.26 Å to 3.22 Å, respectively. This reduction in the bond length between the alloying atom (Ca, Y, and Gd) and Mg-1 atom points to the creation of a local covalent character due to interatomic charge localization. Thus, our results correlate well with the observed higher solute–vacancy binding and vacancy formation energies in Mg–X–Zn ternaries.

From a solute diffusion point of view, a more positive binding energy between the solute and the vacancy sites indicates the solute atom movement toward the vacancy. This reduces the jump distance between the solute and the vacancy sites and lowers the migration energy for that particular jump.15,40 Like in the solute and solute–Zn combinations mentioned above. Since the alloy is rich in Mg (low solute concentration ~1 at. %), Mg–vacancy jumps—specifically between basal planes—will likely determine dislocation climb during creep. Thus, we have examined only Mg–vacancy exchanges and have calculated and compared migration and activation energies in binary and ternary systems. Finally, Fig. 4 illustrates the role of electron localization on diffusion behavior of an Mg atom. Figure 5 shows that such an Mg atom experiences such a variation in bonding environment during a jump event (see purple colored Mg atom in Fig. 6).

### B. Vacancy migration energy in Mg alloys

There are two primary vacancy diffusion paths in hcp-Mg—out-of-plane (OOP) and in-plane (IP) as shown in Fig. 1. We have calculated migration energy barriers (see Table IV) for these paths.
(see Fig. 5) using the NEB method in 96 atom supercells of binary Mg–X (Ca, Y, and Gd) and ternary Mg–X–Zn systems. Activation energy of diffusion, which is the sum of vacancy formation energy and migration energy barrier, is shown in Table IV. We find that the activation energies are roughly inversely proportional to the binding energies of X and X–Zn (see Fig. 2). This is consistent with literature reports with higher binding energy corresponding to lower activation energies. We will discuss migration energetics and the relevant bonding characteristics for binary Mg–X (Sec. III B 1) and ternary Mg–X–Zn (Sec. III B 2) solid solutions, respectively.

1. Binary Mg–X (Ca, Y, and Gd) alloys

Figure 5 shows that OOP migration barriers are invariably higher than corresponding IP vacancy migration. Table IV shows that the addition of these solutes substantially increased the OOP migration barrier energies compared to pure Mg, while a marginal increase in IP barrier was noted. The substantial increase in the OOP diffusion barriers as compared to IP diffusion barriers in binary Mg alloys is now analyzed qualitatively in terms of charge density distribution ($\Delta \rho$).

Figure 6 compares the $\Delta \rho$ isocharge surfaces for saddle point images along IP and OOP vacancy diffusion paths in binary Mg–X
Note that Δρ of the structures shown here corresponds to the peak value in Fig. 5. A careful inspection of isocharge surfaces for OOP diffusion indicate that the diffusing Mg atom (colored purple in Fig. 6) lie within the region of higher density of charge localization (marked with arrows in the bottom row of Fig. 6), which was not in case for IP diffusion. Thus, for a saddle image of OOP vacancy diffusion, excess Δρ between the solute (Ca, Y, and Gd) and Mg atoms (colored purple in Fig. 6) indicate enhanced contribution from covalent bonds. For saddle image along an IP diffusion path, the bond length is 3.8 Å for the purple colored Mg atom in Fig. 6 for Mg–X (Ca, Y, and Gd), which reduces to 3.1 Å for the OOP path. Such elevated charge density induced stronger and stiffer bond correlates with increased OOP diffusion barrier compared to the IP diffusion barrier. Note that quantitative bond stiffnesses in the binary and ternary systems are presented later.

The diffusing Mg atom (purple in Fig. 6) experiences a varying distribution of electronic charge while moving in- or out-of-plane (see yellow contours in Fig. 6) to its final position. Note that both the solute atom X (Ca, Y, and Gd) and Mg–matrix contribute to such density variations. Therefore, we quantified their combined effect on the bonding character of the diffusing Mg atom by computing its partial density of states (PDOS) by projecting DOS along the angular momentum quantum numbers for s, p, and d orbitals. Figures 7 and 8 shows the PDOS of Mg–X for IP and OOP diffusion, respectively. In each figure, the top, middle, and bottom row refer to the initial, transient saddle point, and the final state images, respectively.

Figures 7 and 8 show that the Mg atom has a predominantly metallic character due to the non-zero value at the Fermi level (EF). However, a closer inspection of s orbital occupancy (blue colored plots in Figs. 7 and 8) revealed a slight "dip" near the EF irrespective of the solute atom type. Such a "dip," akin to a bandgap, is distinctly noticeable in Figs. 7 and 8 for the initial and final states of IP and OOP migration. Such a "bandgap" corresponding to the s orbital is presumably due to the partial covalent bonds experienced by the diffusing Mg atom. In contrast, the saddle states of the diffusing Mg atom along IP and OOP paths showed differences in its electron occupancies near the Fermi level EF (middle row of Figs. 7 and 8). While a "bandgap" was noted for IP diffusion, it was barely noticeable for OOP. This also is indicative of the Mg atom experiencing a change in bonding character along the OOP path but not during IP migration.

We further quantify changes in the s, p, and d orbital electron occupancies of the diffusing Mg atom (purple in Fig. 6) along IP and OOP paths (Tables V and VI). The electron occupancy was computed by integrating each PDOS to EF, which only considers the valence band electrons participating in chemical bonding.

Tables V and VI reveal two key perceptions common to Mg–Ca, Mg–Y, and Mg–Gd binaries. First, the s orbital had the highest occupancy and followed by p for the initial, saddle, and final states. The d orbital electrons primarily reside in the conduction band (or the antibonding states), which can be seen from its higher PDOS for E ≥ EF (see black colored plots in Figs. 7 and 8) and substantially lower occupancies (Tables V and VI). Crucially, the saddle state orbital occupancies for IP and OOP diffusion indicated that s orbital occupancy is directly proportional to the migration barrier while the p orbital occupancy is comparable in both IP and OOP saddle states. The higher s orbital occupancy in the diffusing Mg atom correlates with higher migration energy for the OOP path.
Second, the s and p orbital occupancies also change during diffusion (see Δs and Δp values in Tables V and VI). For both IP and OOP paths, the diffusion from the initial to the saddle state increases s orbital occupancy (Δs > 0) and decreases p orbital occupancy (Δp < 0). The Δs values for OOP migration were 2–2.5 times that for the IP path (see Tables V and VI). These results together with the plot of energy vs reaction coordinate (Fig. 5) indicate that the migration barrier correlates well with increasing s orbital occupancy. Finally, during the migration from saddle point to final state, the s and p orbitals largely recover their initial orbital occupancies while d occupancy mostly remains unchanged. Thus, we find that an Mg atom experiences varying bonding environment during its diffusion.

2. Ternary Mg–X (Ca, Y, and Gd)–Zn alloys

Now, we examine the effect of Zn addition to binary Mg–X (Ca, Y, and Gd) alloys by correlating Zn-induced change in the bonding character with migration energetics. We focus on OOP paths because the IP activation energies are comparable to pure Mg.
TABLE IV. Calculated migration barrier $E_M$ and activation energy $E_A$, in eV, for vacancy diffusion in Mg-X (Ca, Y, and Gd) and Mg–X (Ca, Y, and Gd)–Zn alloys are shown. DFT calculations are from fully relaxed, 96-atom supercells. The number in the bracket indicates approximate percentage change after the addition of Zn.

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>OOP pathway</th>
<th>IP pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Migration barrier (eV)</td>
<td>Activation energy (eV)</td>
</tr>
<tr>
<td>Mg (Pure)</td>
<td>0.39$^{23}$</td>
<td>1.2</td>
</tr>
<tr>
<td>Mg–Ca</td>
<td>0.74</td>
<td>1.55</td>
</tr>
<tr>
<td>Mg–Ca–Zn</td>
<td>0.89 (20%)</td>
<td>1.71 (10%)</td>
</tr>
<tr>
<td>Mg–Y</td>
<td>0.70</td>
<td>1.58</td>
</tr>
<tr>
<td>Mg–Y–Zn</td>
<td>0.85 (21%)</td>
<td>1.83 (16%)</td>
</tr>
<tr>
<td>Mg–Gd</td>
<td>0.72</td>
<td>1.58</td>
</tr>
<tr>
<td>Mg–Gd–Zn</td>
<td>0.87 (21%)</td>
<td>1.99 (26%)</td>
</tr>
</tbody>
</table>

Our results indicate that OOP vacancy migration barriers in ternary Mg alloy systems are higher than corresponding OOP vacancy migration barriers in Mg binaries. The addition of a Zn atom as the first neighbor to substitutional Ca, Y, and Gd solutes in the Mg lattice consistently increased the OOP migration energy in the three ternary alloys when compared to their parent binary alloys studied here. Specifically, the OOP migration energy in Mg–Ca–Zn ternary increased by ~128% compared to the pure Mg and ~90% with respect to only Ca substitution. Mg–Y–Zn ternary similarly showed increased OOP migration energy of ~118% compared to the pure Mg and ~79% with respect to only Y substitution. Finally, Mg–Gd–Zn ternary revealed increased OOP migration energy of ~123% compared to the pure Mg and ~85% with respect to only Gd substitution. In general, the vacancy (Table IV), and, more importantly, substantial (~26%) increases in diffusion activation energies were seen only for OOP diffusion.

FIG. 7. IP migration. PDOS of the diffusing Mg atom (colored purple in Fig. 6) at the initial state (top row), saddle state (middle row), and final state (bottom row) in Mg–X binary alloys are shown. The Fermi level defines the zero of energy are indicated using dotted vertical lines.
FIG. 8. OOP migration. PDOS of the diffusing Mg atom (colored purple in Fig. 6) at the initial state (top row), saddle state (middle row), and final state (bottom row) in Mg–X binary alloys are shown. The Fermi level defines the zero of energy that is indicated using dotted vertical lines.

TABLE V. Occupation numbers of s, p, and d orbitals of the Mg atom for IP vacancy diffusion path in the initial, saddle, and final configurations for three binary Mg–X solid solutions. The electron occupation numbers are obtained by integrating PDOS of the purple Mg atom in Fig. 7 up to Fermi energy.

<table>
<thead>
<tr>
<th>System</th>
<th>Initial state</th>
<th>Saddle state</th>
<th>Final state</th>
<th>Difference</th>
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<tr>
<td></td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>s</td>
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<tr>
<td>Mg–Ca</td>
<td>6.08</td>
<td>4.41</td>
<td>0.50</td>
<td>6.34</td>
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<tr>
<td>Mg–Y</td>
<td>6.08</td>
<td>4.42</td>
<td>0.50</td>
<td>6.29</td>
</tr>
<tr>
<td>Mg–Gd</td>
<td>6.08</td>
<td>4.44</td>
<td>0.50</td>
<td>6.28</td>
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TABLE VI. Occupation numbers of s, p, and d orbitals of the Mg atom for OOP vacancy diffusion path in the initial, saddle, and final configurations for three binary Mg–X solid solutions. The electron occupation numbers are obtained by integrating PDOS of the purple Mg atom in Fig. 8 up to Fermi energy.

<table>
<thead>
<tr>
<th>System</th>
<th>Initial state</th>
<th>Saddle state</th>
<th>Final state</th>
<th>Saddle state – initial state</th>
<th>Final state – saddle state</th>
<th>Final state – initial state</th>
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<tr>
<td></td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>s</td>
<td>p</td>
<td>d</td>
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<tr>
<td>Mg–Ca</td>
<td>6.30</td>
<td>4.64</td>
<td>0.49</td>
<td>6.84</td>
<td>3.77</td>
<td>0.40</td>
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<tr>
<td>Mg–Y</td>
<td>6.33</td>
<td>4.73</td>
<td>0.53</td>
<td>6.92</td>
<td>3.96</td>
<td>0.44</td>
</tr>
<tr>
<td>Mg–Gd</td>
<td>6.38</td>
<td>4.77</td>
<td>0.54</td>
<td>6.95</td>
<td>3.94</td>
<td>0.45</td>
</tr>
</tbody>
</table>

FIG. 9. Comparison of differential charge density dispersion in e/Å³ along the c axis for saddle image of in-plane (top row) and out-of-plane (bottom row) vacancy migration paths in Mg–Ca–Zn, Mg–Y–Zn, and Mg–Gd–Zn alloys are shown. Orange spheres are Mg. Green spheres is a Ca, Y, or Gd atom. Blue sphere is a Zn substitutional atom at a Mg site. Each layer of atom represents the (0002)Mg basal planes.
migration barrier energies follow the trend $E_{OOP}^{Mg} - X(Ca,Y, and Gd) - Zn > E_{OOP}^{Mg} - X(Ca,Y, and Gd) > E_{OOP}^{Mg}$ and $E_{IP}^{Mg} - X(Ca,Y, and Gd) - Zn \approx E_{IP}^{Mg} - X(Ca,Y, and Gd) \approx E_{IP}^{Mg}$ similar to previously studied systems. Next, we rationalize the enhanced migration barriers due to Zn addition by systematically investigating the charge distribution, electron occupancies (DOS), and alteration of bond strength in the presence of Zn and compare them to those in pure Mg and binary Mg–X (see Table IV).

Figure 9 shows the isocharge surfaces in the saddle states of Mg–X (Ca, Y, and Gd)–Zn, where the top and bottom row corresponds to IP and OOP paths, respectively. Here, similar to binary Mg–X, the diffusing Mg atom (in purple) in the OOP path is surrounded by a higher concentration of valence electrons than in IP path. However, qualitatively, the spatial extent of the isocharge surfaces near X and Zn appears to be larger than in the binaries.

To better quantify the effect of Zn on the bonding character, we compare the projected density of states of the diffusing Mg atom. Figures 10 and 11 show the PDOS of the migrating Mg atom (colored purple in Fig. 9) along IP and OOP pathways, respectively, while Tables VII and VIII display the corresponding electron occupancies computed from the PDOS. In Figs. 10 and 11, the top, middle, and bottom rows represent the initial, saddle, and final states, respectively, in the ternary Mg–X–Zn alloys. Their PDOS and IP occupancies share similarities with the binary Mg–X.

**FIG. 10.** IP migration. PDOS of the diffusing Mg atom (colored purple in Fig. 9) at the initial state (top row), saddle state (middle row), and final state (bottom row) in Mg–X–Zn ternary alloys are shown. The Fermi level defines the zero of energy are indicated using dotted vertical lines.
Mg–X systems. For example, we see a “dip” in s orbital occupancies near $E_F$ (indicating covalent character) and observe comparable changes in s, p, and d orbital occupancies (Tables V–VII) during initial–saddle and saddle–final state migration indicating a near constant net occupancy of the orbitals after the completion of migration.

The most significant difference between the bonding characteristics of ternary Mg–X–Zn and binary Mg–X revealed comparing the electron occupancy during OOP migration (compare Tables VI and VIII). During the initial to saddle state along a OOP path in Mg–X–Zn, the s orbital gains an average of ~15% more electrons than in binary Mg–X. The $\Delta p$ approximately remains the same for both systems. The higher s orbital electron occupancy may explain the higher migration and activation barriers required for OOP diffusion in Mg–X–Zn.

Interestingly, unlike IP and OOP migrations of Mg–X and IP for Mg–X–Zn, saddle–final state movement caused a substantial loss in s orbital occupancy (approximately ~50% in comparison to the initial–saddle movement), while the p orbital regains only half of its occupancy lost in the previous step. In other words, the complete initial–final state migration resulted in a net loss of electron occupancy of both s and p orbitals ($\Delta s < 0$ and $\Delta p < 0$, in the last column of Table VIII). This is remarkably different from IP and OOP of Mg–X and IP in Mg–X–Zn, where they largely

**FIG. 11.** OOP migration. PDOS of the diffusing Mg atom (colored purple in Fig. 9) at the initial state (top row), saddle state (middle row), and final state (bottom row) in Mg–X–Zn ternary alloys are shown. The Fermi level defines the zero of energy are indicated using dotted vertical lines.
regained their lost electrons after the jump. Taken together, these results indicated that the presence of Zn creates unfavorable chemical bonding conditions for the diffusion of Mg atoms along the c axis of hcp-Mg.

The higher OOP vacancy migration barrier due to the presence of a Zn atom was further quantified by computing bond stiffness (K) along the (0001) direction in binary Mg–X and ternary Mg–X–Zn alloys (Fig. 12). Figure 12(a) plots [0001] displacement $X_{[0001]}$ of an Mg atom as a function of the corresponding restoring Hellman–Feynman forces $F_{[0001]}$. The straight-line fits in Fig. 12(b) indicate that the displacements are within harmonic limits and allowed us to calculate bond stiffness K via Hooke’s law, $F_{[0001]} = K_{[0001]} \cdot X_{[0001]}$. Figure 12(g) indicates that Zn addition to binary Mg–Ca, Mg–Y, and Mg–Gd increases the stiffness, $K_{[0001]}$, by ~64%, 22%, and 5%, respectively. Crucially, we find that the higher bond stiffness along [0001] in Mg–X (Ca, Y, and Gd)–Zn alloys correlate well with higher OOP vacancy migration barriers in Mg–X (Ca, Y, and Gd)–Zn alloys compared to their binary Mg–X (see Table IV). Our past studies on Mg–Nd and Mg–Nd–Zn systems also indicated that the increased $K_{[0001]}$ was related to Zn-induced change in the bonding character.53

The diffusional creep occurs in metals and alloys typically above 0.5$T_m$. At such elevated temperature, vacancy diffusion along grain boundary controls the creep. The Coble creep rate$^{48}$ can be calculated by knowing the solid solubility of an impurity in the parent lattice at the temperature of interest and the relevant atomic sizes. Therefore, segregation of solutes to grain boundary, twin boundary, and other interfaces play an important role in the creep process. It has been reported in the literature$^{42}$ that Zn and other RE elements segregate to the grain boundary and the twin boundary in Mg alloys. Large atomic size misfit of solute in Mg resulted in a higher tendency for solute to segregate to grain boundaries. Our results indicate that Zn produces local contraction regions as depicted by negative impurity volume whereas Ca, Y, and Gd create tensile regions due to larger atomic radii than an Mg atom (refer to Table II). In the presence of Zn, solute–vacancy binding energy increases while atomic size of solute in terms of impurity volume decreases compared to their corresponding values in Mg binaries (refer to Fig. 2(b)). The atomic size of solute also correlates with their solubility limits in Mg, which manifests as solute atom induced drag effect on grain boundary.45 It has been reported that small amounts of strongly segregating solutes can inhibit the Coble creep by reducing grain boundary diffusivity.44 Taken together, our results indicate that a small amount of Zn additions enhance the solute drag effect on boundary and thereby reduce grain boundary diffusivity and inhibit Coble creep. Though our DFT results are at 0 K, vibrational contribution to free energies can be readily obtained by examining lattice dynamics, where one employs phonon thermodynamics within harmonic or quasi-harmonic approximations to account for the effect of finite temperatures.40 However, the addition of such thermal vibration effects is not expected to change the overall conclusions of this paper but will consume significant computer resources.49

To understand creep in Mg alloys, reliable diffusion data and insights into solute diffusion mechanisms in Mg are important. Diffusion coefficients determined theoretically involve the correlation factors that become important when direct solute migration barriers are significantly smaller than the solvent migration barriers.11 In this study, we focused on solvent–vacancy migration barriers for OOP and IP diffusion in Mg–X (Ca, Y, and Gd) and Mg–X

<table>
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<td>s  p  d</td>
<td>s  p  d</td>
<td>s  p  d</td>
<td>s  p  d</td>
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<tr>
<td>Mg–Ca–Zn</td>
<td>6.00 4.35 0.52</td>
<td>6.31 3.80 0.45</td>
<td>6.01 4.20 0.45</td>
<td>0.31, −0.55, −0.07</td>
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<tr>
<td>Mg–Y–Zn</td>
<td>6.04 4.40 0.52</td>
<td>6.28 3.88 0.46</td>
<td>6.05 4.32 0.50</td>
<td>0.24, −0.52, −0.06</td>
</tr>
<tr>
<td>Mg–Gd–Zn</td>
<td>6.04 4.40 0.52</td>
<td>6.31 3.90 0.47</td>
<td>6.07 4.33 0.50</td>
<td>0.27, −0.5, −0.05</td>
</tr>
</tbody>
</table>
(Ca, Y, and Gd)–Zn alloys using NEB calculations. The barriers follow the trends for Mg–La and Mg–La–Zn systems as well as Mg–Nd and Mg–Nd–Zn systems.20,23 We can infer that OOP vacancy diffusion, necessary for dislocation climb, appears to be the rate determining step of creep in these alloys. In our work, we related the increases in energy barriers to local changes in electronic bonding, especially to the formation of shorter and stiffer bonds with significant local directionality in all the model alloys studied here. Thus, we rationalize that engineering stiffer directional bonds via microalloying additions in Mg is a promising route to dramatically improve their high temperature creep response.

IV. CONCLUSIONS

We used the nudged elastic band method coupled with density functional theory (DFT) based first principles computation to understand how out-of-plane (OOP) and in-plane (IP) vacancy diffusion influences creep deformation in binary Mg–X (Ca, Y, and Gd) and ternary Mg–X (Ca, Y, and Gd)–Zn alloys. In general, the OOP migration barriers along the c axis of hcp-Mg were higher than IP migration along the a axis in all the binary systems studied. However, the OOP barrier increased substantially when the ternary element Zn is the first nearest neighbor to the solute atom “X” in Mg–X binary. Differences in migration barriers energies were correlated with the electron charge densities and density of states, quantitative bond stiffness, vacancy formation, and solute–vacancy binding energies.

The vacancy formation and solute–vacancy binding energies were consistently higher for ternary Mg–X–Zn, in comparison with the binary Mg–X alloys studied, due to local relaxation of vacancy volume. Analysis of charge densities revealed that Zn solute enhanced localization of electron charge along the c axis, and in-between the basal planes of hcp-Mg, substantially more than in the Mg–X binary systems. Such enhanced interplanar charge localization in ternary Mg–X–Zn correlated well with higher bond stiffness values along the c axis. The examination of partial density of states along migration pathways indicated greater occupancy of the s orbitals in the saddle states, which correlated well with a higher activation barrier during OOP migration than in IP in all the systems studied. However, the presence of Zn in the ternary alloys increased the s orbital occupancy of the OOP saddle states significantly, which enhanced their activation barrier compared to the binary systems.

In summary, Zn-induced local relaxation enhanced both charge localization and interplanar bond stiffness and together with larger s orbital electron occupancy inhibits out-of-plane migration in ternary Mg–X (Ca, Y, and Gd)–Zn. Consequently, the combined effect of atomistic mechanisms will restrict non-conservative dislocation movement by impeding out-of-plane vacancy movement and improve the creep resistance of ternary Mg–X (Ca, Y, and Gd)–Zn alloys.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES
