Effect of segregated alloying element on the intrinsic fracture behavior of Mg

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Abstract

The interaction between segregated alloying elements (Al, Li, Sn, Y, and Ca) and three crack systems is investigated in magnesium simple crystal under mode I loading condition. Using molecular statics in the framework of the (modified) embedded-atoms method, the effect of segregated alloying elements on both the fracture behavior and the intrinsic fracture toughness were identified, and analyzed quantitatively in the framework of the Rice's theory for dislocation emission at a crack tip (Rice, 1992. *J. Mech. Phys. Solids* **40** 239-271). In addition, the variations of the critical stress intensity factor as a function of the misfit strain between the alloying element and magnesium are discussed. The results revealed the existence of a transition from cleavage to dislocation emission at a crack tip. Such transition from cleavage to dislocation emission at the crack tip depends on (i) the orientation of the crack system, and (ii) the nature of the alloying element segregated at the crack tip. Furthermore, when analyzed as a function of the misfit strain between the alloying element and magnesium, our data suggest a direct relation between the fracture toughness and the misfit strain, independently of crack orientation. While alloying element with compressive misfit strain enhances the intrinsic fracture toughness of magnesium single crystal, alloying element with tensile misfit strain worsens the intrinsic fracture toughness of magnesium single crystal.

Keywords: Atomistic modeling; (Semi)-empirical potentials; Fracture; Dislocation; brittle-to-ductile transition

1. Introduction

In human medicine, titanium and steels are currently used for the treatment of fractures. However, as these materials are stiffer than bones, stress shielding develops during the first stage of the healing process leading to a possible re-shaping of the bones. To avoid such delay in the patients' recovery, implants made of titanium and steels have to be removed from the patients' body during a second surgery. Alternative implants made of magnesium-based alloys are envisioned as (i) their elasticity properties are comparable to those of the bones and (ii) the second surgery could be avoided owing to the total resorption of the implant into the human body. However, before a switch from titanium and steel to magnesium-based alloys implants occurs in orthopedic medicine, the corrosion resistance of the magnesium-based alloys must be improved (Harrison et al., 2014). Surface coating and alloying elements, out of which, aluminum, zinc, calcium, yttrium and rare earths, were proposed to improve the corrosion resistance of magnesium-based alloys (Li et al., 2008; Wang et al., 2012). Due to the neurotoxic effect of Al (Alvarez-Lopez et al., 2010) and the unknown biological effect of rare earth in

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the human body (Gu et al., 2009), these possible alloying elements need to be studied more extensively to demonstrate their biocompatibility and biosafety in view of their use for controlling the resorption rate of the magnesium-based alloy implant.

As the alloying element should improve the corrosion resistance without altering the alloy's mechanical properties, each time a new alloying element is proposed to improve the corrosion resistance, its effect on the mechanical properties of the experimental magnesium-based alloy needs to be identified. In 2006, Somekawa et al. (2006) examined the effect of the concentration of zinc on the fracture toughness of wrought magnesium alloys. Their data showed an increase of the fracture toughness when increasing the concentration of Zn solute atoms from 0.3 at% to 1.6 at%. Later, systematic studies were performed to analyze the effect of different type of alloying elements on the mechanical properties of polycrystalline magnesium-based alloys by correlating the fracture behavior and the toughness with the segregation energy of the solute element (Somekawa et al. 2013, 2014). By comparison with the behavior obtained for pure magnesium, Somekawa et al. (2013, 2014) reported an increase of the fracture toughness associated with a ductile behavior when considering solute elements with small segregation energy, such as Al and Zn. Inversely, a decrease of the fracture toughness combined with intergranular fracture was reported when considering alloying elements with large segregation energy, such as Ca. Furthermore, as the experimental data reported by Somekawa et al. (2013, 2014) suggest a linear dependency of the fracture toughness to the amount of strain carried by the alloying element, these authors identified the lattice parameter ratio, c/a , as one of the most influential material parameters for enhancing or preventing grain boundary embrittlement in magnesium-based alloys with average grain size from 3-5 μm . However, recent experimental data reported by Somekawa et al. (2015) suggest that the initial average grain size of the alloy must be considered when identifying influential material factors controlling the toughness. For example, the twin boundary segregation energy becomes more dominant than the change in the lattice parameter ratio with chemical composition to describe the evolution of the fracture toughness when increasing the average grain size of the alloys from 3-5 μm to approximately 20 μm .

In the above discussion of the experimental observations, the fracture toughness may result from the presence of defects of different natures (grain boundary, brittle particle, segregated or dilute alloying elements, pores, microcrack) as well as their interactions. As each of these defects individually alter the intrinsic fracture toughness, defined as the ability of a defect-free material containing a crack to resist fracture, establishing the mapping of each individual mechanism to the intrinsic fracture toughness, and identifying the most influential material parameters governing the fracture toughness is critical for selecting a manufacturing route leading to alloys with pre-defined properties. We believe that atomistic modeling in the framework of (semi-)empirical potentials is a powerful method to establish such mappings. However, limited studies reporting on the effect of solute atoms on crack propagation in single crystal were reported. Gordon et al. (2007) analyzed the influence of Ni and Cr as ordered substitutional elements on the fracture behavior of α -Fe using molecular statics in the framework of the embedded-atom method. Although no general trends were obtained, transition from cleavage to crack tip blunting was observed by addition of Cr or Ni for certain orientations, while the reverse transition, from crack tip blunting to cleavage was observed for other orientations. From a qualitative perspective, their data suggested that substitutional Ni or Cr atoms cause energetic heterogeneities favoring bond breaking, and, thus, decreasing the critical stress intensity factor. Furthermore, knowing that the intrinsic fracture behavior on a specific plane depends on the ability of the crystal to nucleate dislocation at a crack tip compared to its ability to cleave (Rice, 1992), Gordon et al. (2009a, 2009b) investigated the change of energy barrier for dislocation nucleation at a crack tip in α -Fe resulting from the presence of heterogeneities in the vicinity of the crack tip. Eleven types of alloying elements were

tested, including Cu, Ni, W, and Mo. Based on their atomistic calculations, Gordon et al. (2009a, b) concluded that the presence of Cu and Ni in the vicinity of the crack tip lowered the energy barrier, while the presence of W and Mo increased the energy barrier. The authors did not, however, correlate (i) the misfit strain between the alloying element and the matrix with the change of energy barrier and (ii) the nature of the solute elements to the fracture toughness and behavior.

The objective of this study is to reveal the effect of segregated alloying element on the intrinsic fracture toughness in magnesium single crystal. The work presented in this manuscript is, thus, aimed at (i) demonstrating whether there is a relation between the critical stress intensity factor of mode-I crack and the misfit strain between the alloying element and magnesium, and (ii) analyzing the relation between the concentration of segregated alloying element and the critical stress intensity factor. To this end, the binding energy mapping of substitutional elements located in the vicinity of a crack tip is calculated for different alloying elements. With the knowledge of the energetic in front of the crack tip, a pre-existing crack system is loaded with different concentrations of alloying elements, and the variation of the critical stress intensity factor is monitored to reveal the effect of the alloying element segregated at the crack tip on the mechanism of crack propagation, and its critical stress intensity factor. The numerical results are discussed with regards to theoretical predictions obtained with the Rice's theory of dislocation emission at a crack tip (Rice, 1992).

In this manuscript, the methodology used (i) to quantify the interaction between substitutional atoms and a crack tip and (ii) to calculate the critical stress intensity factor when a local concentration of substitutional alloying element is considered at the crack tip are given in Section 2, in addition to a review of the existing MgX (X being the type of substitutional atom) semi-empirical potentials available in the literature. In Section 3, numerical data revealing the energetic of substitutional atoms at a crack tip are presented for different types of solute atoms. In addition, the evolution of the critical stress intensity factor is presented as a function of the concentration of segregated atoms at the crack tip. The data are discussed in Section 3 with respect to the change of work of separation and stacking fault energy when considering solute atoms. Concluding remarks are given in Section 4.

2. Methodology

2.1 MgX semi-empirical potentials in the literature

Employed in a computational framework, empirical potentials are suitable to (i) reveal mechanisms to be later observed experimentally (Groh et al., 2010; Groh, 2014), (ii) validate continuum theories (Borovikov et al., 2015; Alam and Groh, 2015), (iii) model the mechanical properties of complex metallic alloys (Rösch et al., 2006, 2009; Liao et al., 2014), or (iv) shed light on the nature of the interactions between defects of different dimensionality (Bacon et al., 2009; Liu and Groh, 2014).

The embedded-atom method (EAM) and its modified version (MEAM) were proposed by Daw and Baskes (1983), and Baskes (1992), respectively. To improve the accuracy of non-bulk properties, Lee and Baskes (2000) extended the MEAM framework by considering interaction up the second nearest-neighbor atoms. In both the EAM and the MEAM frameworks, the total energy, E , of an atomic system is approximated as the sum of the atomic energies, E_i , i.e.

$$E = \sum_i E_i. \quad (1)$$

The energy of atom i consists of the embedding energy F_i , i.e., the amount of energy required to embed an atom at an electronic site represented by an average background electronic density, ρ_i , and a perturbation given by the pair potential term, Φ , as follows:

$$E_i = F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \Phi_{ij}(r_{ij}), \quad (2)$$

where j is any neighboring atom of i , and r_{ij} is the distance between atoms i and j . From the energy formulation, thermodynamics forces and stress tensors for the atoms in the lattice are calculated.

From the literature, MgX potentials were proposed for solute elements of Al, Li, Sn, Ca, and Y using the MEAM framework (Kim et al., 2009; Kim et al., 2012; Groh, 2015; Kim et al., 2015) and for solute elements of Al and Li using the EAM formalism (Liu and Adams, 1998; Mendelev et al., 2009; Karewar et al., 2014). For each potential, the domain of application of the Mg-X pair is summarized in Table 1. While the magnesium MEAM potential of Kim et al. (2009) was used as a starting point for Kim et al. (2012), Kim et al. (2015), and Groh (2015) to develop the cross-pair with Al, Li, Sn, Y, and Ca, the magnesium EAM of Sun et al. (2006) was used as a starting point by Mendelev et al. (2009) and Karewar et al. (2014) to develop the cross-pair with Al and Li, respectively. For simplification, G-MEAM, K-MEAM, K-EAM, L-EAM, and M-EAM refer to the potentials proposed by Groh (2015), Kim et al. (2009, 2012, 2015), Karewar et al. (2014), Liu and Adams (1998), and Mendelev et al. (2009), respectively.

Table 1. Application domain for the MgX potentials in the literature.

Potential	X	Domain of application
Liu and Adams (1998)	Al	Segregation energy, and fracture.
Kim et al. (2009)	Al	General physical properties in view of modeling the mechanical behavior of Mg-Al alloys.
Mendelev et al. (2009)	Al	Thermal properties for solid and liquid phases on the Al-rich part of the Al-Mg phase diagram.
Kim et al. (2012)	Li	General physical properties in view of modeling the mechanical behavior of Mg-Li alloys.
Karewar et al. (2014)	Li	Simulations of complex microstructures that include multi-phase regions, segregation at the interfaces and dislocation–precipitate interactions.
Kim et al. (2015)	Ca	General physical properties in view of modeling the mechanical behavior of Mg-Ca alloys.
Groh (2015)	Ca	Heat of formation and elasticity of several MgCa compounds containing different concentrations of Ca. Effect of Ca solute solution on the stable and unstable stacking fault energies of different slip systems.
Kim et al. (2015)	Sn	General physical properties in view of modeling the mechanical behavior of Mg-Sn alloys. As a consequence of a discrepancy between the effects of Sn on the unstable stacking fault predicted by the potential and the effects obtained from first-principles, special attention is necessary when analyzing the effect of Sn on the mechanical behavior of Mg-Sn alloys.
Kim et al. (2015)	Y	General physical properties in view of modeling the mechanical behavior of Mg-Y alloys.

The bulk substitutional formation energy, the ratio of lattice parameter for element X with respect to Mg, and the ratio of c/a of element X compared to Mg are compared in Table 2. One can observe from Table 2 that when substitution in an hcp Mg matrix occurs, solute elements of Al and Li provide a tensile misfit strain while solute elements of Sn, Y, and Ca are at the origin of a compressive misfit strain.

Table 2. Bulk substitutional formation energy, E_X^f , ratio of lattice parameter of element X with respect to Mg, a_X/a_{Mg} , lattice parameters ratio, and c/a , of element X compared to Mg.

	Al ^[1]	Al ^[2]	Al ^[3]	Li ^[4]	Li ^[5]	Sn ^[6]	Y ^[6]	Ca ^[6]	Ca ^[7]
E_X^f (eV)	0.05	0.40	0.09	-0.08	-0.11	-0.35	-0.35	-0.13	-0.24
a_X/a_{Mg}	0.882	0.894	0.883	0.969	0.981	1.072	1.136	1.227	1.229
$\frac{(c/a)_X}{(c/a)_{Mg}}$	1.067	1.025	1.045	1.010	1.004	1.007	0.976	1.016	1.012

[1] Liu and Adams, 1998. [2] Mendeleev et al., 2009. [3] Kim et al., 2009. [4] Kim et al., 2012. [5] Karewar et al., 2014; [6] Kim et al., 2015; [7] Groh 2015.

2.2 Binding energy

To evaluate the interaction between substitutional atoms and a crack tip, we applied a methodology that was previously presented by Bhatia et al. (2014) to investigate the interaction between point defects and edge dislocations in α -Fe, and by Reddy and Groh (2016) to demonstrate Ca alloying element segregates at grain boundaries in nanopolycrystalline magnesium. The substitutional binding energy at a location X_x , $E_b^{X_x}$, is essentially the substitutional formation energy at the location X_x , $E_Z^{X_x}$, minus the bulk formation energy, E_Z^f :

$$E_b^{X_x} = E_Z^{X_x} - E_Z^f, \quad (3)$$

where Z is the type of substitutional element.

The substitutional formation energy at location X_x is given by:

$$E_Z^{X_x} = E(Mg_{n-1}Z) - E(Mg_n) + (E_c^{Mg} - E_c^Z), \quad (4)$$

where $E(Mg_{n-1}Z)$, $E(Mg_n)$, are the total energies of Mg crystallized in the hcp crystal structure with and without one substitutional atom of type Z. E_c^{Mg} and E_c^Z are the cohesive energy/atom ratios of Mg and Z, respectively.

In the present work, the formation energies were characterized for solute elements of Al, Li, Sn, Ca, and Y by using a minimization method based on the second gradient algorithm following a Polak-Ribière implementation. In addition, the binding energy for substitutional atoms in front of the crack tip was calculated for the different types of solute elements.

2.3 Fracture calculation

To reveal the contribution of solute elements on the intrinsic fracture toughness of Mg single crystal, mode-I analysis was performed by means of energy minimization in the framework of the MgX-(M)EAM potentials using the LAMMPS package (Plimpton, 1995). The data were analyzed and visualized using the OVITO package (Stukowski, 2010). An atomically sharp crack oriented in such a way that the crack direction, the crack plane normal, and the crack front coincide with the x_1 , x_2 , and x_3 directions, respectively, was inserted in a cylinder of radius R by displacing the atomic locations according to:

$$\mathbf{x}_i = \mathbf{X}_i + \mathbf{u}(\mathbf{X}_i), \quad (5)$$

where x_i is the position of the atom “ i ” in the crystal containing the crack, X_i is the position of the same atom in the perfect crystal, and $\mathbf{u}(X_i)$ is the displacement of the atom in the cracked crystal as obtained using the mode-I field obtained from anisotropic linear elastic fracture mechanics under plane strain conditions. For an anisotropic elastic solid, with the initial crack tip at the origin, the displacements, $\mathbf{u}=(u_1, u_2)$, are defined by (Cheung and Yip, 1994):

$$u_1 = \Delta K_I \sqrt{\frac{2r}{\pi}} R \left\{ \frac{1}{(\mu_1 - \mu_2)} [\mu_1 p_2 \sqrt{\cos\theta + \mu_2 \sin\theta} - \mu_2 p_1 \sqrt{\cos\theta + \mu_1 \sin\theta}] \right\} \text{ and} \quad (6)$$

$$u_2 = \Delta K_I \sqrt{\frac{2r}{\pi}} R \left\{ \frac{1}{(\mu_1 - \mu_2)} [\mu_1 q_2 \sqrt{\cos\theta + \mu_2 \sin\theta} - \mu_2 q_1 \sqrt{\cos\theta + \mu_1 \sin\theta}] \right\}, \quad (7)$$

where

$$r = \sqrt{x_1^2 + x_2^2}, \text{ and } \theta = \tan^{-1} \left(\frac{x_2}{x_1} \right). \quad (8)$$

In Equations 6 and 7, ΔK_I represents the increment of stress intensity factor for mode-I crack. The distance r and the angle θ provide the location of any atoms in the model relative to the location of the crack tip. μ_1 and μ_2 are complex numbers derived from the elastic compliance constants. p_1 , p_2 , q_1 , and q_2 are complex numbers that can be derived as a function of μ_1 and μ_2 . The operator R denotes the real part of a complex number.

The compliance constants are calculated via the inverse of the elastic constants. When considering an arbitrary orientation of the crack system, the elastic compliance in the oriented reference system is given by:

$$S_{ijkl} = \sum_{mnop} T_{li} T_{jn} S_{mnop} T_{ko} T_{lp}, \quad (9)$$

where S_{ijkl} and s_{mnop} are the compliance constants in the oriented and in the reference systems, respectively. T_{ij} denotes the components of the rotation matrix that transforms the reference system into the oriented frame.

As shown in Figure 1A, the cylinder of radius R was divided into two coaxial regions passing through the location of the crack tip. The radius of the inner cylinder is R_{in} , and the thickness of the outer region is $R - R_{in}$. During the molecular statics loading, the atomic positions located in the inner cylinder of radius R_{in} were minimized using a conjugate gradient algorithm, whereas the atomic locations located in the outer region of thickness $R - R_{in}$ were moved rigidly according to Equations 6 and 7. For all calculations, the increment of displacement, $\Delta \mathbf{u}$, was proportional to an increment of stress intensity factor, ΔK_I , of magnitude $0.001 \text{ MPa}\sqrt{m}$. The atoms from the inner region were assumed to be in a position of minimum energy, when either of the following stopping criteria of the conjugate gradient relaxation algorithm was satisfied: (i) the change in energy was lower than 10^{-14} eV or (ii) the mean gradient per atom was lower than $10^{-14} \text{ eV/\AA}$.

Figure 1. (A) The coordinate system with the definition of the angle θ of the plane through the crack front coinciding with the x_3 axis. (B) The three crystal orientations, I, II, and III, with respect to the crack.

As one objective of this work is to reveal how segregated alloying element at the crack tip affects the fracture behavior and the critical stress intensity factor, a preliminary study to evaluate the critical stress intensity factor in pure magnesium was performed. The critical stress intensity factors for the three crack systems were calculated by performing large-scale simulations in the K-MEAM, M-EAM, and L-EAM frameworks. In these calculations, the initial crack configurations were obtained by simultaneously displacing the atoms according to Equations 6 and 7 with an initial increment of stress intensity factor equal to 80% of the theoretical minimum stress intensity factor, and deleting the atomic interactions between the two crack surfaces. The theoretical stress intensity factors for dislocation emission at the crack tip, and cleavage, reported in Table 3 were evaluated using the Rice's theory of dislocation emission at a crack tip (Rice, 1992) and the unstable stacking faults, shear moduli, Poisson ratios, and surface energies calculated with K-MEAM, M-EAM, and L-EAM. Furthermore, the crack tip position was defined at the location of the atom with the maximum opening stress normalized by the tensile strength obtained from the traction-separation curves (Groh and Alam, 2015). The position of the crack tip as defined with the above criterion was in agreement with the visual location of the crack tip through visualization of the animation once the calculation was completed. As a preliminary result obtained in pure magnesium, apart from the crack system III modeled with L-EAM, the propagation of the crack by cleavage was obtained for the crack systems independently of the potential. As reported in Table 3, cleavage occurred for the crack system I at a critical stress intensity factor of $0.271 \text{ MPa}\sqrt{m}$, $0.191 \text{ MPa}\sqrt{m}$, and $0.241 \text{ MPa}\sqrt{m}$ using K-MEAM, M-EAM, and L-EAM, respectively. For crack system II, cleavage occurred at a critical stress intensity factors of $0.272 \text{ MPa}\sqrt{m}$, $0.214 \text{ MPa}\sqrt{m}$, and $0.253 \text{ MPa}\sqrt{m}$ when considering K-MEAM, M-EAM, and L-EAM, respectively. Furthermore, cleavage took place at $0.288 \text{ MPa}\sqrt{m}$, $0.202 \text{ MPa}\sqrt{m}$ with K-MEAM and M-EAM, and dislocation emission happened at $0.252 \text{ MPa}\sqrt{m}$ with L-EAM, when considering the crack system III. The magnitude of the critical stress intensity factors obtained by direct large-scale calculations of crack propagation is in good agreement with the prediction obtained using Rice's theory for which the stress intensity factors for both cleavage and dislocation emission at the crack are summarized in Table 3. However, although Rice's theory predicts dislocation emission at the tip of crack of systems II and III when considering K-MEAM, this behavior is not recovered when performing large-scale calculation of crack propagation. Wu and Curtin (2015b) already reported similar observations. However, such discrepancy with the theoretical prediction of Rice is not critical in the current study as its objective is to reveal the effect of a local concentration of solute elements on the fracture behavior, with fracture behavior in pure magnesium being the reference. Furthermore, since only the Mg-MEAM potential proposed by Kim et al. (2009) predicts dissociated edge and screw dislocation comparable to those found via density functional theory (Ghazisaeidi et al., 2014), special attention must be given to the

data obtained with the Liu and Adams (1998), Mendelev et al. (2009), and Karewar et al. (2014) MgX potentials for crack system I.

Table 3. Summary of the considered crack systems, and identification of the possible dislocation activity at the crack tip. K_{Id} and K_{Gr} represent the critical stress intensity factor for dislocation emission at the crack tip and cleavage, respectively, predicted by Rice's theory. K_{Ic} is the critical stress intensity factor predicted by large-scale simulations.

Crack	Crack front/plane	Slip system	Critical stress intensity factor, $MPa\sqrt{m}$								
			K-MEAM			M-EAM			L-EAM		
			Theoretical		MS	Theoretical		MS	Theoretical		MS
			K_{Id}	K_{Gr}	K_{Ic}	K_{Id}	K_{Gr}	K_{Ic}	K_{Id}	K_{Gr}	K_{Ic}
I	$[\bar{1}010](0001)$	PyII	0.324 ^h	0.274 ^b	0.271	x ^c	0.155 ^d	0.191	0.291 ^e	0.235 ^f	0.241
II	$[\bar{1}010](\bar{1}2\bar{1}0)$	Basal	0.244 ^a	0.285 ^b	0.272	0.188 ^g	0.186 ^d	0.214	0.244 ^g	0.243 ^f	0.253
III	$[\bar{1}010](11\bar{2}2)$	Basal	0.280 ^a	0.289 ^d	0.288	0.239 ^g	0.184 ^d	0.202	0.268 ^g	0.249 ^d	0.252

^a Using the unstable stacking fault reported by Wu et al. (2015a).

^b Using the surface energy reported by Kim et al. (2009).

^c Nogaret et al. (2010) reported that M-EAM does not predict an unstable stacking in the pyramidal II plane.

^d Using surface energy calculated in this work.

^e Using the unstable stacking fault reported by Nogaret et al. (2010).

^f Using the surface energy reported by Johansen et al. (2009).

^g Using the unstable stacking fault reported by Yasi et al. (2009)

^h Using the unstable stacking fault calculated in this work.

3. Numerical results

3.1 Binding energy mapping in the crack tip vicinity

To verify the reliability of the semi-empirical potentials in describing the interaction between the alloying element and a crack tip, as well as to characterize the nature of the interaction, the binding energy fields of different type of alloying elements (Al, Li, Ca, Sn, and Y) near the crack tip were calculated. While Figures 2A and 2B show the binding energy mapping for substitutional Ca obtained for the crack system I ($[\bar{1}010](0001)$) calculated with G-MEAM and K-MEAM, respectively, Figures 3A and 3B show the binding energy mapping for substitutional Al obtained for the same crack system and calculated with K-MEAM and M-EAM, respectively. For the cases depicted in Figures 2 and 3, the crack tip is located at (0, 0), while the mapping is given along the direction of the crack propagation, $[\bar{1}2\bar{1}0]$, and the normal to the crack plane, $[0001]$.

(A)

(B)

Figure 2. Binding energy mapping in the vicinity of the tip of crack I obtained when substituting Mg by Ca in the MEAM framework calculated with (A) G-MEAM and (B) K-MEAM.

For both elements, the overall binding energy mapping appears to be potential independent. In the case of substitutional Ca, the binding energy was found to be minimum at the crack tip, and it increased with increasing the distance between the substitutional Ca and the location of the crack tip. The minimum binding energy was found in the order of -0.12 eV. Inversely, in the case of substitutional Al, the binding energy was maximized at the crack tip and it decreased with increasing the distance between the crack tip and the location of the substitutional Al. Such a difference in binding energy profile between substitutional Al and substitutional Ca results in different types of interaction between the crack and the substitutional element. While the interaction is attractive in the case of substitutional Ca, the interaction is repulsive when considering substitutional Al. Similar types of interaction were observed when considering the mapping of the binding energy for crack systems II and III. Furthermore, the mapping of the binding energy for substitutional Al calculated using L-EAM was found to be similar to the mapping reported in Figure 3.

Figure 3. Binding energy mapping in the vicinity of the tip of crack I obtained when substituting Mg by Al calculated with (A) K-MEAM and (B) M-EAM.

While the mapping of the binding energy calculated for Ca using K-MEAM and G-MEAM is representative of the ones obtained for Sn and Y calculated with K-MEAM, significant differences were observed on the mapping of the binding energy calculated with K-MEAM and K-EAM when considering substitutional Li. As reported in Figure 4, the analysis of the binding energy suggests the presence of a repulsive force between the crack tip and substitutional Li when considering K-MEAM, whereas the binding energy calculated with K-EAM suggests the presence of an attractive force between the crack tip and substitutional Li. Such a difference in the binding energy mapping when considering substitutional Li modeled with the K-MEAM and K-EAM potentials may be attributed to the small misfit strain between Li and Mg as reported in Table 2. Therefore extra care must be given when analyzing the effect of substitutional Li on the fracture toughness. While Figure 4 was obtained for crack system II, similar mappings of the binding energy when considering substitutional Li were obtained for crack systems I and III modeled in the framework of K-MEAM and K-EAM.

Figure 4. Binding energy mapping in the vicinity of the tip of crack II obtained when substituting Mg by Li calculated in the (A) K-MEAM and (B) K-EAM framework.

From the analysis of the binding energy field of alloying element near the crack tip using different semi-empirical potentials, we can conclude that modeling the interaction between a cloud of segregated Ca, Sn, Y, and Li and a crack tip is realistic in magnesium. However, as shown in Figure 4, the interaction between Li and a crack tip in magnesium single crystal depends on the nature of the semi-empirical potential (K-MEAM vs K-EAM). As a consequence, further work using density functional theory may be necessary to reveal the true nature of the interaction between Li and a crack tip in magnesium single crystal. On the other hand, the analysis of the binding energy field of Al near a crack tip revealed that segregation of a small concentration of Al near a crack tip is unrealistic. However, to have more data in view of identifying a trend between the intrinsic fracture toughness of magnesium single crystal and the misfit strain, the interaction between a small concentration of segregated Al alloying element near a crack tip is still considered in this study.

The initial configuration was obtained by minimizing the total energy of the system when considering Ca, Sn, Y, and Li (when using K-EAM) substitutional elements, and by maximizing the total energy of the system when considering Al and Li (when using K-MEAM) alloying element. Such a strategy is envisioned to reveal the maximum contribution of a local concentration of alloying element in the vicinity of the crack tip on the fracture toughness of magnesium single crystal. However, the exact location of the alloying elements with regards to the crack surface and the possible slip system was not analyzed.

3.2 Effect of segregated alloying element on the intrinsic fracture behavior of Mg

For the three different crack systems considered in this study, the nature of the fracture behavior is summarized in Table 4. As K-EAM and M-EAM do not predict an unstable stacking fault on the pyramidal II plane along the direction $1/3[11\bar{2}3]$ (Nogaret et al., 2010), the qualitative data obtained with these two potentials were not reported in Table 4. Moreover, as the properties of basal dislocations are not well described in the L-EAM framework (Groh et al., 2009), the results obtained with this potential are also not discussed. From the large-scale simulations of crack propagation, it was observed that addition of Ca, Al, or Li does not affect the nature of the crack propagation, while addition of Y or Sn at the crack tip results in a transition from cleavage to dislocation emission at the crack tip. Such observations are valid for crack systems I and II. Transition from cleavage to dislocation emission at the crack tip was observed independently of the nature of the substitutional element when considering the crack system with orientation III.

Table 4. Summary of the crack tip behavior as a function of the orientation, type of substitutional atoms, and number of substitutional atoms in the vicinity of the crack tip. Letters B and E refer to brittle behavior and dislocation emission at the crack tip, respectively.

Orientation	I			II			III		
# of alloying elements at the crack tip	0	5	10	0	5	10	0	5	10
Ca G-MEAM	B	B	B	B	B	B	B	B	E
Ca K-MEAM	B	B	B	B	B	B	B	E	E
Y K-MEAM	B	B	E	B	B	E	B	E	E
Sn K-MEAM	B	E	E	B	E	B	B	B	E
Al K-MEAM	B	B	B	B	B	B	B	E	E
Li K-MEAM	B	B	B	B	B	B	B	E	E

Figure 5. Snapshot representing the opening strain, ϵ_{yy} , extracted from the simulations illustrating the growth behavior of a crack in the crack system I when considering two concentrations (A) five substitutional Ca atoms and (B) ten substitutional Ca atoms in the vicinity of the crack tip.

Figures 5, 6, and 7 illustrate the effect of substitutional elements at the crack tip on the nature of the crack propagation obtained for crack systems I, II, and III, respectively. As reported in Table 4, the addition of Ca alloying elements at the crack tip does not alter the nature of the crack propagation for crack systems I and II. This finding is illustrated in Figures 5A and 5B with two different concentrations of Ca atoms at the crack tip. It is shown that independently of the local concentration of Ca solute atoms at the crack tip (five and ten Ca solute atoms for Figures 5A and 5B, respectively), the analysis of the opening strain, ϵ_{yy} , reveals the same behavior, i.e., crack propagation by cleavage. Such qualitative behavior appeared to be potential independent as similar trends were obtained with K-MEAM and G-MEAM. When increasing the local concentration of Y alloying element at the tip of crack systems I and II (by increasing the number of alloying elements from five to ten), a transition from cleavage to dislocation emission is reported in Table 4. Such transition is clearly identified when analyzing the shear strain, ϵ_{yx} , as illustrated in Figure 6. While the shear strain is constant when considering five Y substitutional atoms in the vicinity of the crack tip (see Figure 6A), the presence of a sheared region with its origin at the crack tip is observed when considering ten Y substitutional atoms at the crack tip. As represented by the insert of Figure 6B, a basal dislocation dissociated into two Shockley partials separated by a stacking fault I_2 is observed at the end of the shear region.

Figure 6. Snapshot extracted from the simulation representing the shear strain and illustrating the growth behavior of a crack from the crack system II when considering two different concentrations (A) 5 atoms and (B) 10 atoms of substitutional Y in the vicinity of the crack tip. The insert in (B) shows the local crystal structure near the dislocation based on a common neighbor analysis (blue, green, and gray atoms are crystallized in hcp, fcc, and unknown crystal structures, respectively).

When considering crack system III, transition from cleavage to dislocation emission at the crack tip was observed by performing large-scale calculations as reported in Table 4. Such transition from cleavage to dislocation at the crack tip is independent on the nature of the alloying element at the crack tip. In the case of Ca alloying elements at the crack tip, the transition occurred with low and high local concentrations when considering K-MEAM and G-MEAM, respectively. The analysis of the shear strain, ϵ_{yx} , revealed the transition from cleavage to dislocation emission at the crack tip, as illustrated in Figure 7. As shown by shear strain in Figure 7, dislocation gliding was observed on a plane oriented at 58° compared to the crack plane. By performing a common neighbor analysis, it appeared that the dislocation is dissociated into two Shockley partials separated by an intrinsic stacking fault I_2 as shown by the insert of Figure 7.

Figure 7. Snapshot extracted from the simulation representing the shear strain and illustrating the emission of dislocation at the tip of a crack of orientation III when considering a local concentration of Ca alloying elements in the vicinity of the crack tip. The insert shows the local crystal structure around the dislocation based on a common neighbor analysis (blue, green, and gray atoms are crystallized in hcp, fcc, and unknown crystal structures, respectively).

To quantitatively analyze the effect of alloying element segregated at the crack tip on the nature of crack propagation, both the surface energies and the unstable stacking fault energies were calculated with the different potentials when considering 25% of solute elements distributed uniformly on the surface, and 25% of solute elements distributed uniformly on the plane adjacent to the stacking fault, respectively. Although such concentrations would, most likely, lead to precipitation in engineering

alloys, it provides a framework for comparison of the results with first-principles calculations. In addition, we verified that the increase/decrease of the surface/unstable stacking fault energies varies monotonically with increasing the concentration of substitutional atom on the surface and on the plane adjacent to the stacking fault.

The decrease and increase of the unstable stacking fault energy on the basal plane along the $[\bar{1}010]$ reported by Kim et al. (2015) was recovered with K-MEAM by addition of Y and Sn on the plane adjacent to the stacking fault, respectively. On the other hand, our calculation revealed an increase of the unstable fault energy from 125 mJ/m^2 to 151 mJ/m^2 using K-MEAM when considering 25% of Ca on the plane adjacent to the stacking fault while Kim et al. (2015) reported a decrease of the unstable stacking fault from 126 mJ/m^2 to 112 mJ/m^2 using the same configuration. The same configuration resulted in a decrease of the unstable stacking fault energy from 125 mJ/m^2 to 108 mJ/m^2 using the G-MEAM framework. When considering Li as substitutional element in the K-MEAM framework, the unstable stacking fault energy is decreased by 13 mJ/m^2 compared to the value obtained in the pure magnesium. Finally, our calculations revealed that the unstable stacking fault energy on the basal plane along the direction $[\bar{1}010]$ is unaffected by Al. By comparison with the first-principles data reported by Moitra et al. (2014a, and b), we conclude that Ca (G-MEAM), Y (K-MEAM), and Li (K-MEAM) alloying element predict the same variation of unstable stacking fault energy, while Ca (K-MEAM) and Sn (K-MEAM) alloying element predict the opposite trend.

Similarly, the addition of Ca, Y, and Li on the adjacent plane to the pyramidal second order plane resulted in a decrease of the unstable stacking fault energy on the pyramidal second order plane along the direction $\langle 11\bar{2}3 \rangle$ when considering G-MEAM and K-MEAM. While the addition of Ca in the G-MEAM framework decreases the unstable stacking fault energy by 37 mJ/m^2 compared to the value obtained in the pure magnesium, addition of Ca, Y, and Li decreases the unstable stacking fault energy by 15 mJ/m^2 , 1 mJ/m^2 , and 5 mJ/m^2 , respectively, when considering K-MEAM. The observed decrease of the unstable stacking fault by addition of Ca, Y, and Li is in agreement with the first-principles predictions of Moitra et al. (2014b). The addition of Al increases the unstable stacking fault energy on the pyramidal second order slip plane along the direction $\langle 11\bar{2}3 \rangle$ by 20 mJ/m^2 when considering K-MEAM, which is in disagreement with the first-principles prediction of Moitra et al. (2014b).

Finally, our calculations revealed a decrease of the (0001) surface energy by addition of Ca, Sn, Li, and Al, independently of the nature of the potential. In addition, the presence of 25% of Y alloying element on the surface increases the (0001) surface energy by about 30% compared to the value obtained for pure magnesium. Similar results were obtained when considering the $(\bar{1}2\bar{1}0)$ and the $(11\bar{2}2)$ surface energies. It should be noted that variations of the surface energy by the presence of alloying element on the surfaces are predictions of the model that would need to be confirmed using first-principles calculations.

By combining the surface energy and the unstable stacking fault energy obtained in the presence of alloying element with the Rice's theory of dislocation emission at a crack tip, the critical stress intensity factors for cleavage, K_{Gr} , and dislocation emission at the crack tip, K_{Id} , were estimated. The variations of the ratio K_{Id}/K_{Gr} for the different types of elements are plotted in Figure 8. The ratio K_{Id}/K_{Gr} for pure magnesium obtained with the K-MEAM is given in Figure 8 for comparison purposes.

Figure 8. Effect of 25% of X solute atoms on the ratio K_{Id}/K_{Gr} when the surface and stacking energies are calculated with 25% of alloying distributed uniformly on the surface, and on the plane adjacent to the stacking fault, respectively.

As reported in Figure 8, with the exception of Y, the substitution of 25% of magnesium atoms by alloying elements on the plane adjacent to the stacking fault and the surfaces results in an increase of the ratio K_{Id}/K_{Gr} compared to the one obtained for pure magnesium when considering crack systems I and II. Therefore, according to Rice's theory, the addition of solute atoms at the crack tip enhances crack propagation by cleavage. When considering Y alloying elements, the substitution of 25% of Mg atom by Y atoms results in a decrease of the ratio K_{Id}/K_{Gr} from 1.18 and 0.856 to 0.99 and 0.61 for crack system I and II, respectively. Thus, according to the Rice's theory of dislocation emission at a crack tip, the addition of Y alloying elements enhances dislocation emission at the crack tip. As a consequence, a transition from cleavage to dislocation emission is possible according to Rice's theory. Although the transition from cleavage to dislocation emission at the crack tip is confirmed using the Rice's theory, further validation of the variation of the surface energy in the presence of Y has to be confirmed using first-principles calculations. With the exception of Sn, the substitution of 25% of magnesium atoms by alloying elements on the plane adjacent to the stacking fault and the surfaces results in a decrease of the ratio K_{Id}/K_{Gr} compared to the one obtained for the pure magnesium when considering crack system III. Therefore, the substitution of 25% of magnesium atoms by alloying elements on the plane adjacent to the stacking fault and on the $(11\bar{2}2)$ surface enhances the transition from cleavage to dislocation emission at the crack tip when considering crack with orientation III as illustrated in Figure 7, and reported in Table 4.

Finally, the type of event occurring at the crack tip when considering substitutional Sn strongly depends on the nature of the crack system. Thus, for crack system II, while crack propagation occurs by cleavage in the pure magnesium, large-scale calculations revealed dislocation emission and cleavage when considering five and ten substitutional Sn atoms at the crack tip. Such observations suggest that both the surface energy and the unstable stacking fault energy do not vary monotonically with the concentration of Sn. When calculating the surface energy and the unstable stacking energy with different concentrations of substitutional Sn uniformly distributed on the surface and on the plane adjacent to the stacking fault (3.1%, 6.25%, 12.5%, and 25%, respectively), both the surface energy and the unstable stacking fault varied monotonically, and, therefore, no transition from cleavage to dislocation emission can be predicted in the framework of Rice's theory. However, as the effect of Sn on the magnitude of unstable stacking fault prediction obtained with K-MEAM does not follow first-

principles calculations, the justification of the qualitative crack propagation behavior revealed by large-scale calculation cannot be explained based on Rice's theory of dislocation emission at the crack tip.

3.3 Relation between fracture toughness and misfit strain

One objective of this work is to reveal whether there is a relation between the fracture toughness and the misfit strain between the alloying element and magnesium. Figure 9 shows the evolution of the normalized critical stress intensity factor calculated for the alloy MgX as a function of the misfit strain obtained for crack systems I, II, and III.

Figure 9. Evolution of K_{IC}^X/K_{IC}^{Mg} as a function of the misfit strain between the alloying element and magnesium for (A) crack system I, (B) crack system II, and (C) crack system III.

For each type of alloying element (Al, Li, Sn, Y, and Ca) considered in this work, two different local concentrations were considered in the vicinity of the crack tip: five and ten solute atoms. Independently of the local concentration and independently of the crack system, the data summarized in Figure 9 suggests the presence of a relation between the misfit strain and the critical stress intensity factor. When considering a single crack under mode-I in magnesium, the addition of Al, Li, Sn, Y, and Ca alloying elements in the vicinity of the crack tip alters the alloy's resistance to crack propagation. Unlike the data reported by Somekawa et al. (2013) which revealed a decrease of the fracture toughness when considering Ca, Y, Sn, and Al, the addition of Ca, Y, Sn, and Li alloying elements in the vicinity of the crack tip increases the fracture toughness compared to the one obtained in pure magnesium, independently of the crack system. When considering a local concentration of Al alloying elements in the vicinity of the crack tip, large variations of fracture toughness were obtained depending on the nature of the potential. However, as M-EAM and L-EAM are not sufficiently accurate

frameworks to model $\langle a \rangle$ and $\langle c+a \rangle$ dislocations in pure magnesium, it can be concluded that a local concentration of Al alloying elements in the vicinity of the crack tip leads to a decrease of the fracture toughness. It should, however, be noted that a direct comparison between the trend revealed by Somekawa et al. (2013) and the trend revealed in this work is not straightforward as the relation between the fracture toughness and the misfit strain revealed in the current work is performed on single crystal, while the trend between the fracture toughness and the lattice parameter c/a revealed by Somekawa et al. (2013) is valid for polycrystalline materials, where different fracture mechanisms are involved, such as enhancement of intergranular fracture when increasing the lattice mismatch between the solute elements and the host leading to a decrease of the fracture toughness.

4. Concluding remarks

In this work, molecular statics calculations in the framework of the (modified)-embedded-atom method were performed to reveal the effect of segregated alloying elements on the intrinsic fracture toughness of magnesium single crystal, and to identify whether or not there is a relation between the critical stress intensity factor and the misfit strain between the alloying element and magnesium. Alloying elements of Ca, Sn, Y, Li, and Al were considered in this work. Properties such as binding energy and misfit strain when embedded in a magnesium matrix were considered to characterize the nature of the alloying element, and to segregate alloying element at the crack tip. Using such characterization, the misfit strain between alloying element and magnesium increases when considering alloying elements in the following order: Ca, Y, Sn, Li, and Al. When simulating the propagation of mode-I crack with different orientations, our large-scale calculations of mode-I crack propagation revealed a possible change of mechanism occurring at the crack tip due to the presence of a segregated alloying element, leading to a brittle-to-ductile transition. Apart from Sn for which the potential does not reproduce accurately the change of unstable stacking fault energy, the origin of the brittle-to-ductile transition was analyzed in the framework of the Rice's theory for dislocation emission at the crack tip. A good agreement between Rice's theory predictions and the data obtained through large-scale calculations was found. Furthermore, for the three crack systems analyzed in this work, the data obtained by large-scale simulations revealed a clear relation between the critical stress intensity factor and the misfit strain.

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