Direct observation of solute interstitials and their clusters in Mg alloys

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ABSTRACT

Individual solute interstitial atoms in Mg alloys were directly observed through aberration-corrected Z-contrast imaging. The atomic species and local positions of solute interstitials were further determined in combination of density functional theory calculations based on their formation energy. Individual octahedral and tetrahedral interstitials in hexagonal-close-packed Mg are Zn and Y, respectively. Interestingly, there are six positions around the center of each octahedral interstice, which can also accommodate a Zn interstitial, besides the ideal octahedral interstice. Y tetrahedral interstitials evolve to [0001] Y-Mg dumbbells. Moreover, an Y atom can form a crowdion between two neighboring Mg atoms along the $\langle 20\bar{2}3 \rangle$ direction. In particular, small clusters consisting of various point defects were observed, providing direct evidence for enthalpy-driven clustering of point defects, which may have implications for atomic-scale understanding of nucleation mechanisms of strengthening precipitates.

1. Introduction

Interstitials have important influences on various properties of materials [1–6]. Octahedral and tetrahedral interstitials are the mostly studied ones in metals and alloys so far [1,4,6–8]. A crowdion is a kind of interstitial with an atom inserted between two neighboring matrix atoms along a close-packed direction, instead of at the center of an interstice; and its center of mass can easily move along that axis, according to simulations [9]. Impurity interstitials can act as obstacles for dislocation motion; when they form atmospheres along dislocations, serrated flow, dynamic strain aging may occur during plastic deformation of metallic materials [10–12]. Large atoms prefer to substitute for matrix metal atoms, according to the Hume-Rothery rule. However, some large impurity atoms could diffuse even faster than small non-metal atoms in hexagonal close packed (HCP) metals, such as Fe, Co and Ni in Ti and Zr [4]. The anomalously fast mobility of relatively large impurity metal atoms was attributed to an interstitial-mediated diffusion mechanism [1,4], which may have potential applications on synthesis and processing of materials. The addition of a thin Ni foil between two Ti plates to be joined was able to greatly improve the weld quality [13]. Nucleation and growth of precipitates in metal matrix usually involves relocation of atoms from their original lattice sites to interstices, such as precipitates of Laves phase MgZn_2 and icosahedral quasicrystal $\text{Zn}_6\text{Mg}_3\text{Y}$ in Mg alloys [14].

It is thus important to study interstitials, in order to understand mechanisms underlying materials performances, such as strengthening,

diffusion and solid-state phase transformations, which are closely associated with interstitials. Numerous theoretical modeling and computer simulations have been carried out about the structure and property of interstitials [1,8,15]. But, direct visualization of individual interstitials can provide useful knowledge about local atomic structures of the defects in materials, which is very helpful for understanding their dynamics and function [16–18]. Aberration-corrected scanning-transmission electron microscopy (STEM) is able to image single heavy dopant atoms with an atomic number, Z , larger enough than the matrix atom, whether they were at the surfaces or embedded in the bulk lattice [19]. For example, substitutional atoms of Sb in Si were observed by high-angle annular dark field (HAADF) STEM imaging [20]. But, direct observation and identification of interstitials and crowdions in multi-component alloys are still challenging.

Zn is an important alloying element in many Mg alloys [14,21–26]. And addition of rare-earth elements in Mg alloys may improve their ductility and creep resistance [27,28]. In this work, we studied Zn and Y interstitials in Mg alloys through combining aberration-corrected HAADF-STEM experimental observations and density functional theory (DFT). Besides conventional interstitial structures, including octahedral interstitials of Zn and Y-Mg [0001] dumbbells, Zn interstitials can also occupy positions slightly deviating from the ideal octahedral interstices, while individual Y atoms can exist as crowdions. Importantly, local clustering of interstitials was observed. Direct observation and identification of solute interstitials and their clusters may provide useful information for in-depth understanding and modeling a variety of

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phenomena closely associated with point defects, such as diffusion, solute segregation and nucleation of precipitates, as well as their influences on the materials' performances.

2. Materials and Method

Binary Mg-2Zn and ternary Mg-1Zn-2Y (atomic %) alloys were prepared by high frequency induction melting in a graphite crucible under argon atmosphere. Samples for electron microscopy observations were prepared by standard Ar ion milling. Samples were thinned to perforation by 3.5 keV Ar ions, followed by surface cleaning at 0.5 keV. HAADF-STEM observations were performed on an aberration-corrected Nion UltraSTEM 100 microscope operated at 60 kV which is below the threshold (~ 90 kV) for displacement damage in Mg [29,30]. A beam convergence half-angle of 30 mrad was used, which provided a focus depth of about 4 nm [31]. A detector half-angle range of 86–200 mrad was used to record HAADF-STEM images. Atomic resolution imaging was usually performed in regions with a sample thickness below 20 nm, according to measurements of electron energy loss spectroscopy. Image simulations were performed using a package based on a multislice algorithm [32].

First-principles calculations were performed with density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package [33]. The electron exchange and correlation were described with the generalized gradient approximation of Perdew, Burke and Ernzerhof [34] and the electron-ion interaction was represented by the projector augmented wave method [35], with plane wave up to an energy cutoff of 350 eV. The formation energy of a model containing m Mg atoms and l , n interstitial Zn, Y atoms was calculated by

$$\Delta E_f = E(\text{Mg}_m\text{Zn}_l\text{Y}_n) - mE(\text{Mg}) - lE(\text{Zn}) - nE(\text{Y}),$$

where $E(\text{Mg}_m\text{Zn}_l\text{Y}_n)$ is the total energy of interested defect configurations, and $E(X, X = \text{Mg}, \text{Zn}, \text{Y})$ is the energy of per X atom in its bulk. To eliminate the unusual size dependence of formation energy calculation, large supercells containing $5 \times 5 \times 4$ Mg unit cells were used, with the theoretical lattice constants of $a = 3.209$ and $c = 5.120$ Å for HCP Mg.

3. Results and Discussion

Fig. 1 shows positions for two types of widely discussed interstitials, an octahedral interstitial (OI) and a tetrahedral interstitial (TI), in HCP crystals schematically, which will be used to identify the type of interstitials observed by HAADF-STEM imaging. Besides OI and TI, there may be other six symmetrical interstitial configurations, such as [0001] dumbbell (DB), crowdion (C), basal split, basal crowdion, basal octahedral, basal tetrahedral [36].

First-principles calculations show that the formation energies of both Zn (-0.03 eV/atom) and Y (-0.09 eV/atom) substitutions are negative (Table 1). This is consistent with experimental observations of atomic columns showing enhanced brightness omnipresent in all Mg grains observed by HAADF-STEM (see one example shown by the profile overlapped on Fig. 2(a)). Interestingly, intensity spots at non-lattice sites were also observed in Mg grains of both alloys. Fig. 2 shows atomic resolution HAADF-STEM images recorded along the $\langle 1\bar{2}10 \rangle$ Mg zone axis for the Mg-Zn-Y alloy. There are extra intensity spots at non-lattice positions like these indicated by circles and squares in HCP Mg lattice, which was never observed in pure Mg samples (Supplementary Fig. S1). Interestingly, coexistence of several non-lattice intensity spots was observed more frequently (Fig. 2(c) and (d)), compared with single ones (Fig. 2(a)). The brightness of one Zn or Y atom is roughly 5 or 8 times that of a Mg atom in HAADF-STEM images [19]. These intensity spots indicated by circles and squares are attributed to OI and TI atoms (Fig. 1), respectively. The extra intensity spot indicated by an arrow in Fig. 2c implies presence of a solute crowdion out of the HCP basal plane. The intensity spots indicated by rhombuses in Fig. 2(d) are resulted from solute atoms at positions deviating slightly from tetra-

Fig. 1. Schematic models showing interstitials of OI and TI in HCP structures viewed along: (a) a direction close to $[1\bar{2}10]$ and (b) $[0001]$, respectively. The TI atom is along with a Mg column viewed along the $[0001]$ zone axis.

Table 1

Calculated formation energies, E_f (in eV) of substitutionals (Sub), interstitials and crowdions in Mg.

	Sub	OI	TI	C	OID	3Zn + 1Y
Zn	−0.03	1.15	1.57	1.32	1.12	5.39 ^a
Y	−0.09	3.27	2.87 ^b	2.97	3.18	
Mg	−	2.39	2.33 ^b	2.19	−	

^a 3Zn OIDs + 1Y-Mg DB.

^b Y-Mg or Mg-Mg DB.

hedral interstices. Additionally, the Mg column indicated by an arrow in Fig. 2(d) shows an intensity spot with an extended tail, suggesting presence of a solute atom at its immediate vicinity close to an octahedral interstice marked by the dashed circle. The observed interstitials and crowdions should not be produced by knock-on damage, since the high tension applied is below the threshold value for Mg [29]. Atomic species of these point defects cannot be readily and accurately determined directly from the STEM images, since the corresponding intensity depends not only on the atomic number of the solute atom, but also its depth in the sample [19].

Fig. 2. (a) One octahedral interstitial (○). (b) One octahedral interstitial and one tetrahedral interstitial (□). (c) One octahedral interstitial, one tetrahedral interstitial, and a crowdion indicated by a white arrow. (d) Three octahedral interstitials, two interstitials (◊) deviating slightly from tetrahedral interstices, and the Mg column indicated by an arrow showing a tail pointing to an octahedral interstice. There is no visible intensity from single Mg atoms (□) of Y-Mg dumbbells in (b) and (c). In (d), the spot indicated by double circles (◎) is resulted from two Zn OIs, showing higher intensity than the other two (○) for single OIs. There are Mg columns showing obviously higher brightness in all images due to presence of substitutional solute atoms, e.g., the leftmost peak of the intensity profile overlapped on (a).

First-principles calculations show that formation energies of an OI and a TI of Zn are respectively 1.15 eV and 1.57 eV (Table 1), implying that Zn would form OIs (Fig. 3(a) and (c)) instead of TIs. Y would form TIs which evolve into a [0001] Y-Mg DB finally (Fig. 3(e)), according to DFT calculations. Therefore, those extra spots indicated by circles and squares on HAADF-STEM images shown in Fig. 2 are attributed to the presence of octahedral Zn and tetrahedral Y interstitials, respectively. The single Mg atom of an Y-Mg [0001] dumbbells could not produce visible intensity on HAADF-STEM images (Figs. 2(b), (c) and 3(e)). The intensity spots from the Y atoms of the Y-Mg DBs are usually higher than those from Zn OIs in the same region, since the atomic number of Y ($Z = 39$) is higher than Zn ($Z = 30$). This is also confirmed by image simulations (Fig. 3(a) and (e)). Additionally, based on the calculated formation energies, it is deduced that the possibility for the presence of an Y crowdion is about 15 times that of a Zn crowdion in a Mg-Zn-Y solid solution, according to the Boltzmann equation of statistical thermodynamics [37]. Therefore, crowdions in the Mg-Zn-Y solid solution are likely scattered Y atoms (Figs. 2(c) and 3(f)). Presence of crowdions was only predicted theoretically in previous studies [9]. Our atomic resolution observations provided direct evidence for the formation of individual crowdions in HCP metals experimentally.

Individual Y tetrahedral interstitials in Mg will evolve into Y-Mg dumbbells (Fig. 3(e)). However, it was observed that there were two TIs which were not in the DB configuration at a region with also several Zn interstitials below them, as indicated by rhombuses in Fig. 2(d). This configuration was confirmed by first-principles calculations (Fig. 3(g)). The presence of three Zn OIs in Mg makes it hard for the Mg atom on

top of them to deviate from its HCP lattice site obviously (Fig. 3(g)). Therefore, an Y interstitial atom would stay at a position nearby a tetrahedral interstice, if several neighboring Zn OIs were present in HCP Mg lattice (Figs. 2(d) and 3(g)). At the same time, the strain field from the Y interstitial made the Zn interstitials deviating from the octahedral interstices to some extent. The left Zn interstitial shown in Fig. 3(g) is close to the neighboring Mg atomic column, which might result in the appearance of an extended tail of the intensity spot for the Mg column (Fig. 2(d)).

Interestingly, first-principles calculations show that isolated Zn interstitials deviating slightly from octahedral interstices (OIDs) (Fig. 3(b) and (d)) have a formation energy 0.03 eV lower than that of an ideal Zn OI in Mg. There are six positions with a point group of $\bar{3}$ around the center of an octahedral interstice in Mg. The decreased formation energy of OIDs is thus associated with their higher multiplicity of 6, compared with a multiplicity of 1 for OIs in HCP metals, according to theory of statistical thermodynamics [37]. This little difference in formation energies between OIs and OIDs of Zn implies similar concentrations for these two kinds of interstitials in Mg-Zn solid solution, considering the uncertainty of about 0.05 eV of the calculated energies. A Zn OID is at a position quite close to one edge of a triangle connecting three neighboring Mg atoms in a basal plane viewed along [0001] (Fig. 3(d)). This theoretical prediction was confirmed by experimental observations, as shown in Fig. 4. There are respectively one and six intensity spots from OIDs in regions shown in Fig. 4(a) and (c), as indicated by triangles. Presence of interstitials with low-symmetry configurations was also predicted by first-principles calcula-

Fig. 3. (a) and (c) Zn OI viewed along $\langle 1\bar{1}0 \rangle$ and $[0001]$, respectively. (b) and (d) Zn OI viewed along $\langle 1\bar{1}0 \rangle$ and $[0001]$, respectively. (e) and (f) $\langle 1\bar{1}0 \rangle$ projections of an Y-Mg $[0001]$ DB and one Y crowdion, respectively. (g) Relaxed configuration for co-existence of three Zn OIDs and one Y TI ($3\text{Zn} + 1\text{Y}$) in Mg. The Mg atom of the Y-Mg DB is originally at a lattice site shared by the three Mg octahedra holding the three Zn interstitials. Overlapped on defect models shown in (a) and (e) are simulated images for a Zn OI and an Y-Mg DB in samples of 5.2 nm thick, without consideration of local lattice distortion around the point defects.

tions in other HCP metals, such as Ti, Zr and Hf [8]. Those extra intensity spots indicated by circles on HAADF-STEM images (Fig. 4(a) and (c)) are thus associated with Zn OIs. Although first-principles calculations (Table S1) indicated that Zn might form basal octahedral interstitials, since the formation energy is quite close to that of normal OIs, basal octahedral interstitials have not been observed so far experimentally.

The formation energy for the complex defect structure consisting of three Zn interstitials and one Y-Mg DB (Fig. 3(g)) is 5.39 eV which is almost 1.0 eV lower than the sum (6.32 eV) of formation energies of the four isolated defects. Therefore, interstitials and crowdions within a local region might segregate to form clusters, which is driven by decrease of local energy [38,39], as shown in Figs. 2 and 4. In fact, larger clusters with more interstitials were also observed experimentally in both alloys. Fig. 5(a) shows an atomic resolution HAADF-STEM image for a region with a high density of point defects including Zn OIDs, Y-Mg DBs and one Y crowdion in the Mg-Zn-Y alloy. Shown in Fig. 5(b) is a region containing high density of Zn OIDs in the Mg-Zn alloy. Furthermore, there are two or more Zn OIDs at different depths for positions indicated by black triangles in Fig. 5(b), according to their higher intensities compared with those indicated by red ones.

Individual interstitials and crowdions of large atoms are high energy defects (Table 1). Therefore, isolated Zn or Y interstitials were seldom observed in regions without substitutional and/or interstitial Zn/Y atoms in the same local region (Fig. 2). But, our atomic resolution observations provided direct evidence for the enhanced stability of small clusters containing solute interstitials and crowdions in HCP Mg. First-principles calculations demonstrate that clustering of point defects is driven by decrease of enthalpies (Fig. 3 and Table 1). Our atomic-

scale observations of tiny clusters of solute interstitials in Mg provide pertinent evidence for enhanced stability of clusters of point defects previously observed by molecular dynamics simulations and low-magnification phase contrast observations [15,39]. Computer simulations found that interstitial atoms did not recombine with vacancies at the periphery of tiny dislocation loops formed by self-interstitials [15]. Interestingly, coarsening of interstitial dislocation loops in α -Fe, instead of shrinkage, was observed through phase-contrast imaging in a transmission electron microscope during in situ heating experiments [39].

In addition, compositional fluctuations are usually omnipresent in real alloys. There are always atomic columns with Zn or Y substitutional atoms at positions where solute interstitials were observed experimentally (Figs. 2, 4, 5, and see Fig. S2 for a much larger region), implying that the formation energies for solute interstitials within local regions enriched in Zn and/or Y would be decreased to some extent below the calculated ones (Table 1), which benefited the formation of solute interstitials. Local structural transformations would occur through reorganization of atoms, if the chemical composition within a region reached a level sufficient for stabilizing a structure different from the matrix [40]. The observed small clusters containing solute interstitials/crowdions with enhanced stability might be embryos which could trigger formation of strengthening precipitates in Mg grains.

4. Conclusion

In summary, we have observed Zn and Y interstitials in HCP Mg by aberration-corrected HAADF-STEM imaging. Zn atoms may form OIs or

Fig. 4. (a, c) Atomic resolution HAADF-STEM images recorded along [0001] in the Mg-Zn alloy, showing presence of extra intensity spots at positions close to the mid-point of the dashed edges of triangles. Circles indicate intensity spots from OIs. (b, d) Schematic models corresponding to the structures shown in (a) and (c), respectively. The arrow in (a) points to a Mg column with Zn substitutional atom(s). No lattice distortion is taken into account in the schematic models for simplicity.

OIDs in Mg, while Y atoms may exist as Y-Mg dumbbells or crowdions out of basal planes. The formation of Zn OIDs and Y crowdions was demonstrated experimentally with atomic resolution for the first time. More importantly, solute interstitials or crowdions were often found in

configurations of small clusters, in good agreement with the reduced formation energies from DFT calculations. Our investigations show how powerful it is to combine atomic resolution Z-sensitive microscopy imaging with DFT calculations in studying point defects and their tiny

Fig. 5. Atomic resolution HAADF-STEM images showing presence of clusters consisting of solute atoms. (a) Zn OIDs (Δ), Y-Mg DBs ($\square$), one Y TI ($\circ$) and one Y crowdion indicated by an arrow in the Mg-Zn-Y alloy observed along $\langle 1\bar{1}2 \rangle$, (b) Zn OIDs (Δ) in the Mg-Zn alloy observed along [0001]. In (b), spots in red triangles show intensities slightly lower than the surrounding Mg columns, suggesting the presence of single Zn OIDs within the focused depth of the sample; black triangles highlight spots showing intensities much higher than those indicated by red triangles, demonstrating presence of two or more Zn OIDs at different depths; the spot in the circle was produced by a Zn OI. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

clusters in multicomponent materials, which may provide important information for understanding many solid-state processes on the atomic level.

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