Atomistic simulations of precipitation hardening mechanisms in Mg-Al alloys

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Abstract. Precipitation hardening of Mg-Al alloys primarily comes from the interaction of basal dislocations with Mg$_{17}$Al$_{12}$ precipitates. Strengthening of Mg-alloys by precipitation is much less efficient than in other metallic alloys (e.g. Al) and this behaviour has been attributed to geometrical effects, as the Mg$_{17}$Al$_{12}$ precipitates grow as thin plates/lozenses or long rod shape parallel to the basal plane. In the present study I focus on the dislocation/precipitate interaction in the athermal limit for both edge and screw type basal dislocations, carried out using molecular statics methodology. In particular, the critical resolved shear stress (CRSS) necessary to overcome the precipitates are determined as a function of the precipitate size and compared with predictions of classical continuum models. These results provide valuable information about the precipitate hardening mechanisms and suggested new avenues to improve the mechanical properties of Mg-Al alloys.

1. Introduction
Magnesium alloys have become one of the most promising materials in automotive industries due to its high specific strength (158 kN-m/kg), biodegradability, and abundance [1]. Currently further use of Mg-alloys in structural applications is restricted due to various metallurgical issues including strength, formability, limited ductility at room temperature, corrosion, creep resistance and fatigue fracture [2, 3, 4]. It is well known that the deformation mechanism of hexagonal closed pack (hcp) Mg is fundamentally different from that of their fcc (face centered cubic) counterparts, because of their anysotropyness in different slip systems [5, 6]. Strengthening of Mg-alloys are typically done either by solute hardening or precipitate hardening [7, 8]. Within the traditional physical metallurgical understanding, small precipitates are cut by the dislocations, and larger ones are impenetrables, thus facilitate the growth mechanism [9, 10]. Accordingly, the precipitate growth kinetics has a direct relationship in hardness vs aging time relation [9, 11]. While the precipitation strengthening is less effective in Mg-alloys as compared to the Al-alloys, it is not clearly understood whether the
shortcoming is from the precipitate hardness itself or from the matrix-precipitate morphology or from the incipient plasticity, based primarily on basal slip and twinning [12, 13].

The growth of these precipitates in matrix usually preferred in some particular orientations, known as orientation relationship (OR). Out of several reported ORs for lath-shaped or lozenge-shaped precipitates, the most found OR is (0001)\textsubscript{m}∥(011)\textsubscript{p} and [2-1-10]\textsubscript{m}∥[1-11]\textsubscript{p} [14]. A few of these precipitates are also found in rod shaped, where the long axes are either parallel to [0001] or at a certain small angle to [0001]. These rod shaped precipitates are having an OR of [0001]\textsubscript{m}∥[111]\textsubscript{p} and (1-100)\textsubscript{m}∥(1-11)\textsubscript{p} [15]. It is reported that these rod shaped precipitates are more efficient in strengthening the Mg-Al alloy, in comparison to plate-shaped precipitates [12, 13]. However, no studies has been done particularly to understand the precipitation hardening for two different orientations of precipitates that are distributed either in lozenge or rod shape in Mg-matrix. Accordingly, in this paper we show the effect of two different orientations of the precipitates in hardening Mg-Al alloys. In the present paper we calculate the critical resolved shear stress (CRSS) for a basal edge and screw dislocation in Mg to overcome a precipitate of 9 different sizes (2 nm–10 nm), oriented differently in the Mg-matrix, as found in experiment, within athermal limit.

Atomistic simulations of the interaction of a basal dislocations with Mg\textsubscript{17}Al\textsubscript{12} precipitates were carried out using the open-source parallel molecular dynamics code LAMMPS [16] using Mendelev’s EAM (Finnis-Sinclair type) [17] as the formation energy prediction of this potential is closest to the density functional theory (DFT) calculations [18].

Figure 1: Simulation cells for atomistic simulations of basal dislocation/precipitate interactions. The precipitate has a disk shape and is parallel to the (0001) plane. (a) Edge dislocation. (b) Screw dislocation. The crystallographic orientation and the cell dimensions are indicated in the figure. Shear stresses were applied to the atoms on the top surface while the atoms at bottom surface are fixed.

The simulation box (Fig. 1) was parallelepipedic and the X, Y and Z axes were parallel to the [11-20], [10-10] and [0001] orientations of the HCP Mg lattice. The dimensions of the box were 48 × 33 × 21 nm\textsuperscript{3}. They were chosen following the results of Szajewski and Curtin [19] to minimize the image stresses for the number of atoms (≈1.8 millions) in the simulation box. A dislocation (edge or screw) and a Mg\textsubscript{17}Al\textsubscript{12} cylindrical precipitate with a given size and orientation were introduced in the simulation box (Fig. 1). The dislocation line was always parallel to the Y axis. The atom positions corresponding to the HCP lattice of Mg were first generated in desired crystallographic orientations. The edge edge dislocation was included by deleting a half-plane of atoms on the (11-20) plane using ATOMSK [20]. In the case of the screw dislocation, the crystallographic orientation of the simulation
box was \( X \parallel [-1010], Y \parallel [1120] \) and \( Z \parallel [0001] \) (Fig. 1). ATOMSK was also used to introduce a screw dislocation by applying the \( a \) displacement in the plane normal to the dislocation line to all the atoms assuming isotropic elasticity. The precipitates have a disk shape with 3 nm in height. A void of these dimensions was created in the cell and the atom positions of the \( \beta \text{Mg}_{17}\text{Al}_{12} \) precipitates following the ORs \( [0001]\text{Mg} \parallel [110] \beta \) or \( [0001]\text{Mg} \parallel [111] \beta \) were generated and introduced in the void. The basal plane of the Mg lattice was parallel to the disk and the dislocation line was aligned with the midsection of the precipitate disk. The whole simulation cell was relaxed again using the conjugate gradient algorithm and the equilibrium distance between the edge of the precipitate and the dislocation line was approximately 2 nm.

The position of the six layers of atoms at the bottom surface remained fixed during the simulations while six layers of atoms at the top surface were fixed along their normal direction \( Z \) and constrained to two-dimensional displacements in the \( XY \) plane. Incremental displacements of 0.02 nm were applied to the atoms at the top surface along the \( X \) axis in order to move the dislocation. The conjugate gradient method was used to minimize the energy of the system after each incremental displacement. The shear stress \( \tau_{xz} \) induced by the incremental displacement eventually led to the dislocation movement along the \( X \) axis, and the dislocation glide was hindered by the precipitate. The volume-averaged stress tensor \( \sigma_{\alpha\beta} \) was calculated by using Virial definition without the kinetic energy contribution according to [21]

2. Results and Discussions

The atomistic model presented above is used to analyze the basal dislocation-precipitate interaction in the athermal limit as well as the critical resolved rhear stress necessary to overcome the precipitate for the two precipitate ORs. The \( \text{Mg}_{17}\text{Al}_{12} \) precipitates were approximated by circular disks with a diameter in the range 2 nm to 10 nm and a constant height of 3 nm. Interaction of both edge and screw dislocations with the precipitates was ascertained for each precipitate orientation and diameter.

The interaction of a basal edge dislocation with a precipitates with the OR \( [0001]\text{Mg} \parallel [110] \beta \) is shown in Fig. 2 for precipitates of 8 nm in diameter. In both cases, the \( X \) axis (horizontal) was parallel to the [111] direction in the precipitate. All the HCP atoms (Mg-matrix), determined using common-neighbours analysis, were removed from the picture, and only the partial dislocations, stacking fault, and the precipitate are shown. As the dissociated dislocation approaches the precipitate due to the applied shear stress, the leading partial (LP) is attracted, enters and shears the precipitate, as shown in Fig. 2b. Afterwards, the trailing partial (TP) also is attracted and shears the precipitate, becoming closer to the LP, Figs. 2c. The width of the dislocation stacking fault in the Mg becomes narrower around the precipitate when both the LP and TP are within the precipitate and the shape of the LP and TP indicates that the precipitate is an obstacle to the dislocation motion. Finally, the LP overcomes the precipitate but the TP is pinned by the precipitate and it is only able to overcome the precipitate when the TP lines are parallel to the Burgers vector, Figs. 2d. Thereafter, the TPs are also combined, and the full edge dislocation bypasses the precipitate, Figs. 2e. This mechanism was the same in the whole range of precipitate diameters (2 to 10 nm) analyzed and for precipitates with OR \( [0001]\text{Mg} \parallel [110] \beta \) and \( [0001]\text{Mg} \parallel [111] \beta \). The latter are not shown for the sake of brevity.
Figure 2: Progressive shearing of a Mg$_{17}$Al$_{12}$ precipitate of 8 nm in diameter by an edge basal dislocation. The
OR was [0001]Mg $\parallel$ [110]$_{\beta}$ and the X axis (horizontal) was parallel to the [111] direction in the precipitate. The
Y axis is perpendicular to the figure. Atoms in HCP positions are not shown. Green atoms are in FCC positions
while blue atoms are in BCC positions. Precipitate and atoms in unknown positions are grey.

The dislocation/precipitate interactions in the case of a screw dislocation and precipitates with the OR
[0001]Mg $\parallel$ [110]$_{\beta}$ and [0001]Mg $\parallel$ [111]$_{\beta}$ are the same as shown in the Fig. 2 for precipitates of all the
sizes of diameters considered in this study. The dissociated screw dislocation (with a narrower staking
fault, as compared to the edge dislocation) also shears the precipitate and the mechanisms are very
similar to those observed in the case of edge dislocations. The TP is also pinned at the shearing
process, providing most of the drag for the dislocation motion.

Figure 3: Shear stress - shear strain curves from molecular
statics simulations for both edge and screw dislocations.
The OR of the precipitates was [0001]Mg $\parallel$ [110]$_{\beta}$.

The atomistics simulations also provide the shear
stress-shear strain curve during the deformation of
the periodic simulation cell. The curves in Fig. 3
show the mechanical response when precipitates of 2
nm and 8 nm of diameter with OR [0001]Mg $\parallel$ [110]$_{\beta}$
are sheared by edge and screw dislocations,
respectively. The initial region of the curves is linear
and the slope is given by the shear modulus, $\mu =
12.8$ GPa, which is obtained with this atomic potential [37], which is lower than the actual shear
modulus of Mg ($\approx 16$ Gpa). A certain non-linearity in the stress-strain curves is observed afterwards in
the case of the edge dislocations, that corresponds to the shearing of the precipitate for the LP and TP
dislocations (Fig. 2b) and the critical resolver shear stress is attained once the TP overcomes
the precipitate (Figs. 2d). Afterwards, the shear stress decreases as the dislocation exits the precipitate and
the whole process is repeated, due to periodic boundary condition. The curves corresponding to the
screw dislocation are equivalent although the non-linear region during the shearing the precipitate is
missing and the critical resolved shear stress is higher than that for edge dislocations for the same
precipitate diameter.
The critical resolved shear stress (CRSS), $\tau_c$, for edge and screw dislocations in $\beta$ precipitates with OR [0001]$\text{Mg}$$\parallel[110]$$\beta$ are plotted as a function of the precipitate diameter in Fig. 4. These CRSS were obtained when the [111] direction of the precipitate was parallel to the X axis the simulation box but similar values were obtained when the X axis was parallel to the [110] direction of the precipitate. As expected, $\tau_c$ increased with the precipitate diameter and the stress necessary to overcome the precipitate was higher for screw dislocations. As no differences were found in the precipitate shear mechanisms between edge and screw dislocations, the mismatch in $\tau_c$ is not obvious but it cannot be attributed to the nature of Peierls stress of screw dislocations (15 MPa) which is slightly higher than that of edge dislocations ($\approx$ 11 Mpa).

Figure 4: Evolution of the critical resolved shear stress, $\tau_c$, as a function of the precipitate diameter for precipitates with OR [0001]$\text{Mg}$$\parallel[110]$$\beta$. Left panel is for edge and right panel is for screw dislocation case.

Although the precipitates were sheared by the dislocations and no Orowan loops were formed, it is interesting to compare $\tau_c$ with the Orowan stress, $\tau_O = \mu b/(L-d) = 123$ MPa where $b = x.x$ nm is the Burgers vector, $L = 32$ nm the width of the periodic simulation cell and $\mu = 12.8$ GPa the shear modulus coming from atomistic simulations, and $d$ is the corresponding precipitate diameter. Although it can be argued that the actual shear modulus of Mg is higher ($\approx 16.4$ GPa) (and, thus, $\tau_O$ could reach 158 MPa), it was decided to use the shear modulus of the atomistic simulations to compute the Orowan
stress for consistency. Nevertheless, the critical resolved shear stress was higher than the Orowan stress for most precipitate diameters but Orowan loops were never found.

The critical resolved shear stress, $\tau_c$, for edge and screw dislocations in $\beta$ precipitates with OR [0001]$\text{Mg}[\langle111\rangle\beta$ are plotted as a function of the precipitate diameter in Fig. 5. As in the previous case, these results were obtained for precipitates in which the X axis of the simulation cell is parallel to the [110] direction of the precipitate but there were equivalent to those found when the X axis was parallel to the [112] direction. The evolution of $\tau_c$ in Fig. 5 with precipitate size was very similar to that reported in Fig. 4 for $\beta$ precipitates with OR [0001]$\text{Mg}[\langle111\rangle\beta$. However, $\tau_c$ was always higher for a given precipitate diameter and dislocation character in the [111] orientation and the differences were larger in the case of screw dislocations. These differences cannot be attributed due to a change in mechanism but to the stress necessary to shear the precipitate.

The author acknowledges he support from S. N. Bose National Centre for Basic Sciences, Kolkata.

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