Solid Solution Softening Mechanisms in Mg-Ca Alloy

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In the present work, electronic structures of pure Mg, Mg-Ca and Mg-Al alloys were investigated by first-principle calculations. The charge density between the solute and solvent atoms in the Mg-Ca alloy was lower than that in the Mg-Al alloy. The local charge density of states (LDOS) of Mg atom in the Mg-Ca alloy was almost the same as the LDOS of the Mg atom in the pure Mg, suggesting that the solute Ca atoms had little effect on the Mg-Mg bonding in the Mg-Ca alloy. On the other hand, there is more and deeper valley in the LDOS of the Mg atom in the Mg-Al alloy, compared with that in the Mg-Ca alloy, suggesting that the solute Al atom may increase the covalency of the Mg-Mg bonds. A series of the calculations indicates that Ca atoms enhance the formation of double kinks rather than hinder the movement of dislocations, resulting in solid solution softening of Mg-Ca alloy.

Keywords: magnesium, mechanical properties, solid solution softening, first-principles calculation

1. Introduction

To date, many studies have been performed to determine the mechanisms of solid solution hardening, and there are many explanations for solid solution hardening based on dislocation theory including friction mechanisms including elastic modulus interactions,¹¹ chemical interactions,¹² short-range order³ and electrical interactions.⁴ The basis of these mechanisms is the interaction between a solute atom and a dislocation, namely, solute atoms obstruct the movement of dislocations. Meanwhile, it has been reported that in some substitutional Fe alloys,⁵–⁷ the addition of solute atoms results in a reduction in strength, that is, “solid solution softening” occurs. For example, Okazaki⁷ showed that the solute atoms of Ni, Mn, Al and Si give rise to solid solution softening in Fe alloys. Solid solution softening also occurs in Mg-Ca alloy.⁸ Figure 1 shows the stress-strain curves at 123 K for pure Mg, Mg-0.036 at%Ca alloy and Mg-2.7 at%Al alloy. Clearly, the addition of Ca decreases the strength of Mg, while the addition of Al increases its strength. Solid solution softening has been found in Mg alloys⁸–¹³ as well as Fe alloys. Arsenault¹⁴ pointed out the effect of impenetrable point obstacles on the formation of double kinks in solid solution softening. Sato and Meshii¹⁵ showed that solid solution softening is related to the motion of a screw dislocation through a combined field of Peierls potential and misfit strain centers. However, the fundamental understanding of solid solution softening is still insufficient. In the present study, the origin of solid solution softening in Mg-Ca alloy is investigated by performing first-principle calculations, and the criteria for solid solution softening are discussed.

2. Computational Method

The calculations were performed using the Cambridge Serial Total Energy Package (CASTEP),¹⁶ in which density functional theory (DFT)¹⁷,¹⁸ was used with a plane wave basis set to calculate the electronic properties of solids from first principles. We used the Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) to represent exchange and correlation interactions in the DFT. Ultrasoft pseudopotentials¹⁹ were used for all elements in the calculations. All atomic positions were optimized with respect to all structural parameters in accordance with Hellman-Feynman forces and stresses using the Brodyen-Fletcher-Goldfarb-Shanno (BFGS) algorithm.²⁰ The optimization calculations were performed until the convergence criteria were satisfied, that is, 5.0 × 10⁻⁶ eV for the energy change per atom, 0.01 eV Å⁻¹ for the RMS forces, 0.02 GPa for the RMS stress and 5.0 × 10⁻⁴ Å for the RMS displacement. The supercell of pure Mg consisting of 64 Mg atoms, and one solvent atom was substituted by one solute atom for the alloys. The concentration of solute element was 1.563 at% for Mg alloys. The size of Mg supercells prior to relaxation was 12.837 × 12.837 × 10.421 Å. The cutoff energy was set to 350 eV,²¹ which is higher than the default cut-off energies for any elements, for all calculations. The Brillouin zone was sampled using a Monkhorst-Pack k-point grid.²² A 3 × 3 × 4 k-points mesh was used for pure Mg and Mg alloys. The Gaussian smearing with 0.1 eV width was...
used. All calculations of the charge density were performed after optimization of the geometry. The lattice parameters $a$ and $c$ calculated from the pseudopotentials for pure Mg were 3.225 and 5.162 Å. These calculated values are in good agreement with the corresponding experimental values of 3.211 and 5.210 Å. Additional calculations with the 16-atom supercell, the 36-atom supercell and the 64-atom supercell were performed to investigate effects of the cell size on the structural strain due to the presence of the solute atoms, as a result, effects of the cell size were little and the 64-atom supercell was enough for investigating the electronic structure in the Mg alloys.

Also, the (0002) generalized stacking fault energy lines along the (2110) direction were calculated for pure Mg, Mg-Ca alloy and Mg-Al alloy. The generalized stacking fault energy, which was obtained by cutting a perfect crystal with two free surfaces and displacing the two parts relative to each other on the fault vector in the slip plane, was calculated with pure Mg slab, MgCa slab and MgAl slab models. The pure Mg slab model consisted of 10 layers in the (0001) direction and the unit cell contained 40 Mg atoms. Also, the MgCa and MgAl slab models were prepared by substituting one Mg atom adjacent to the slip plane in the pure Mg slab model with one Ca or Al atom. In all the calculations, the atomic positions were relaxed only in the direction perpendicular to the slip plane. The cutoff energy was set to 340 eV and $4 \times 4 \times 1$ k-point grids were used for the pure Mg, MgCa and MgAl slab models. The dependence of supercell was investigated with the models with 8, 10 and 12 layers, and there were minor differences (~1.5%) in the generalized stacking fault energy between the 8 layers and the 10 layers models and between the 10 layers and the 12 layers models. In addition, the Mg-Ca and the Mg-Al bond states were investigated from the local charge density of states (LDOS) of the Ca atom and the Al atom in the Mg alloys, and the Mg-Mg bond states in the Mg alloys were investigated from the LDOS of the Mg atom (Mg1) nearest to the solute atom and the LDOS of the Mg atom (Mg2) located next to the Mg1 atom, where the locations of the Mg1 and the Mg2 atoms are shown in Fig. 2(d).

3. Results and Discussion

The 3-dimension charge density iso-surfaces are shown in Fig. 2(a)–(c) in pure Mg, Mg-Ca and Mg-Al alloys, where the border charge density for the iso-surfaces is 0.072 electrons/Å$^3$. There are more grey color regions around the Ca atoms. This indicates that the charge densities around the Ca atom are lower. The charge density maps on the (0002) and (1100) planes in pure Mg and Mg-Ca and Mg-Al alloys are shown in Fig. 3(a)–(f). The (0002) basal and (1100) prismatic slips play an important role in plastic deformation in Mg. The charge density is lower around the Ca atoms in both the (0002) and (1100) planes in the Mg-Ca alloy. On the other hand, the charge density is higher around the Al atoms in the Mg-Al alloy. Thus, the loose solute-solvent atomic bonding is characteristic of the Mg-Al alloy. The same trend is found in Fe alloys showing solid solution softening. Formation of double kinks and their sideward motion are required for movement of a dislocation. The occurrence of solid solution hardening depends on the velocity of kinks, but solid solution softening is affected by the formation of double kinks. Hence, the loose solute-solvent (Ca-Mg) atomic bonding is likely to enhance the formation of double kinks. The number of valence electrons of the first-neighbor Mg atom to the solute atom was 2.051 for the Mg-Ca alloy and 1.939 for the Mg-Al alloy, although the charge transfer was not unobservable in
Fig. 4 The (0002) generalized stacking fault energy lines along the (2110) direction for pure Mg, Mg-Ca alloy and Mg-Al alloy. The maximum generalized stacking fault energy is 14.19 meV/Å² for the pure Mg slab model, 15.11 meV/Å² for the Mg-Al alloy slab model and 9.88 meV/Å² for the Mg-Ca alloy slab model, respectively.

Fig. 5 The local charge density of states (LDOS) of (a) Mg atom in pure Mg, (b) Ca atom in Mg-Ca alloy, (c) Al atom in Mg-Al, (d) Mg1 atom in Mg-Al alloy, (f) Mg2 atom in Mg-Ca alloy and (g) Mg2 atom in Mg-Al alloy. The Mg1 atom is the Mg atom nearest to the solute atom and the Mg2 atom is the Mg atom located next to the Mg1 atom. The locations of the Mg1 and the Mg2 atoms are shown in Fig. 2(d).

Fig. 3. The charge transfer can be explained from the viewpoint of the electronegativity. Also, the Mg-Ca bond length was larger than the Mg-Mg bond length. These are responsible for the reduced charge density around the Ca atoms.

The (0002) generalized stacking fault energy lines along the (2110) direction are shown in Fig. 4 for pure Mg, Mg-Ca alloy and Mg-Al alloy. The maximum generalized stacking fault energy was 14.19 meV/Å² for the pure Mg slab model, 15.11 meV/Å² for the Mg-Al alloy slab model and 9.88 meV/Å² for the Mg-Ca alloy slab model, respectively. Clearly, the generalized stacking fault energy is reduced by addition of Ca, while it is increased by addition of Al. This agrees the experimental results in Fig. 1.

Figure 5 shows the local charge density of states (LDOS) of (a) Mg atom in pure Mg, (b) Ca atom in Mg-Ca alloy, (c) Al atom in Mg-Al, (d) Mg1 atom in Mg-Al alloy, (f) Mg2 atom in Mg-Ca alloy and (g) Mg2 atom in Mg-Al alloy. As shown in Fig. 5(b), there are few valleys in the LDOS of the Ca atom in the Mg-Ca alloy and the Mg-Ca bond has the metal character. Therefore, it is suggested that when a Mg-Ca bond is broken for the formation of double kinks, the bond breaking does not lead to microcracking, in spite of the loose Mg-Ca bonding, because re-bonding occurs readily. In addition, the LDOS of the Mg1 and the Mg2 atoms in the Mg-Ca alloy are almost the same as the LDOS of the Mg atom in the pure Mg, indicating that the solute Ca atoms have little effect on the Mg-Mg bonding in the Mg-Ca alloy. On the other hand, in the LDOS of the Al atom in the Mg-Al alloy, many deep valleys are found and the Fermi level is located at the relatively deep valley, and therefore the Mg-Al bonding has partial covalent characters. Also, it is observed that there is more and deeper valley in the LDOS of the Mg1 atoms in the Mg-Al alloy (the arrowed line in Fig. 5(e)), compared with that in the Mg-Ca alloy (the arrowed line in Fig. 5(d)), although the difference is not drastic, suggesting that the solute Al atom not only enhances the Mg-Al bonding but also may increase the covalency of the Mg-Mg bonds. This is probably because Al has a character rather intervening between simple metals and covalent materials. Thus, the formation of double kinks and the movement of dislocations are limited by the addition of Al, resulting in solid solution hardening in the Mg-Al alloy. On the other hand, the solute Ca atoms weaken the Mg-Ca bonding, while they have no effect on the Mg-Mg bonding. This leads to the enhanced formation of double kinks and no inhibition of dislocation motion, and therefore, solid solution softening occurs in the Mg-Ca alloy.

There are two other possible mechanisms for solid solution softening in Mg alloys. One is a decrease in the c/a ratio, where c and a are the lattice constants. However, the c/a ratio calculated by first-principle calculations was 1.601 for the Mg-Ca alloy, which is larger than that for pure Mg (= 1.600). Akhtar et al. also noted that a decrease in Peierls’ stress is not associated with the c/a ratio. Therefore, the solid solution softening in the Mg-Ca alloy is not attributed to a decrease in the c/a ratio.

Another possibility is an increase in stacking fault energy because the cross slip is enhanced by an increase in stacking fault energy. In this study, to calculate the basal plane stacking fault energy in pure Mg and the Mg-Ca alloy, supercells with two different structures were used: one had the stacking sequence ABABABACACAC, which is the intrinsic fault I, and the other had the sequence ABABABABABAB. They consisted of 2 Ca and 46 Mg atoms (For pure Mg, all 48 atoms were Mg). A cutoff energy of 350 eV and a 6 × 6 × 2 k-points mesh were used for pure Mg and the Mg-Ca alloy. The stacking fault energy γSF can be given by
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4. Summary

The first-principle calculations showed that solid solution softening in Mg-Ca alloy was due to a decrease in charge density between the solute and solvent atoms. The LDOS of Mg atom in the Mg-Ca alloy was almost the same as the LDOS of the Mg atom in the pure Mg, suggesting that the solute Ca atoms had little effect on the Mg-Mg bonding in the Mg-Ca alloy. On the other hand, there is more and deeper valley in the LDOS of the Mg atom in the Mg-Al alloy, compared with that in the Mg-Ca alloy, suggesting that the solute Al atom may increase the covalency of the Mg-Mg bonds. A series of the calculations indicates that Ca atoms enhance the formation of double kinks rather than hinder the movement of dislocations, resulting in solid solution softening of the Mg-Ca alloy.

REFERENCES


\[ \gamma_{\text{SF}} = \frac{E_{\text{SF}} - E_{\text{bulk}}}{S}, \]  

where \( E_{\text{SF}} \) is the total energy of the supercell with the stacking fault, \( E_{\text{bulk}} \) is the total energy without the stacking fault and \( S \) is the area of the stacking fault. As a result, the calculated stacking fault energies of pure Mg and the Mg-Ca alloy were 3.16 and 0.47 meV/Å², respectively. The addition of Ca significantly decreases the stacking fault energy. Therefore, this mechanism can also be ruled out. In some Mg alloys, a decrease in the c/a ratio or an increase in stacking fault energy can lead to solid solution softening. However, these mechanisms hold only in specific Mg alloys such as Mg-Li alloy.26) Akhtar and Teghtsoonian9–12) showed that solid solution softening occurred in many Mg alloys. The origins for solid solution softening may be different from each other. There are too few data to understand the origins for solid solution softening in the Mg alloys, and further research is needed.

Solid solution softening tends to occur in BCC and HCP metals; however, there have been no reports on solid solution softening in FCC metals to the best of the authors' knowledge. The rate-controlling process for plastic deformation is the movement of screw dislocations for both BCC and HCP metals.30–35) For example, the rate-controlling process of Mg is the cross slip of screw dislocations from the basal plane to nonbasal planes. In BCC and HCP metals, because the Peierls stress for screw dislocations is large, the solid solution softening effect is large. In addition, the solid solution hardening effect is lower in substitutional BCC and HCP alloys than in substitutional FCC alloys since the hardening due to the size effect by substitutional elements is negligibly small in screw dislocations. Therefore, solid solution softening is more apt to occur in BCC and HCP metals than in FCC metals.

One of the features of solid solution softening is its nonoccurrence at elevated temperatures.5,36) In general, the critical resolved shear stress for dislocation movement can be divided into a thermal component and an athermal component. Determinant for the thermal component is whether it is of a short-range field, in which case it can be overcome by thermal activation. On the other hand, determinant for the athermal component is whether it is of a long-range field. As shown in Fig. 3, the marked change in charge density by the addition of a solute is only over a short range, indicating that solute solution softening is a thermally activated process. Therefore, solid solution softening vanishes at elevated temperatures because double kinks can be formed readily by thermal activation. Also, it is of interest to note that solid solution softening occurs upon the addition of a small amount of solute atoms.11,13) The concentration of Ca in the softened Mg-Ca alloy was only 0.036 at%. Also, Blake et al.13) showed that the solid solution softening occurs up to about 0.6 at%. The sideward motion of a kink readily occurs once a double kink is formed.15) Hence, the deformability can be enhanced even when a small number of double kinks are formed. A large concentration of solute atoms may enhance the obstacle of dislocation movement, compared with the formation of double kinks. Therefore, it is suggested that the conditions required for the solid solution softening are a low temperature and a low concentration of solute atoms.