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# The transformation pathways for vitual long period stacking-ordered Mg: First-principles study ☆

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ABSTRACT

The transformation pathways between vitual long period stacking-ordered Mg are investigated using first-principles methods. Two kinds of slip modes, multi-slip-planes mode (M mode) and single-slip-plane mode (S mode), are proposed to calculated the generalized stacking fault energy curves during the transformation process. Based on the energy barriers, the optimized transformation pathways can be obtained. The energy barriers of M mode and S mode are the same for $2H \rightarrow 6H_2$, $6H_1 \rightarrow 6H_2$, $14H_4 \rightarrow 14H_2$ and $14H_4 \rightarrow 14H_5$, respectively. However, the energy barriers of M mode are larger than that of S mode for these transformation with the consideration of vacuum space. For $2H \rightarrow 6H_1$ and $14H_1 \rightarrow 14H_3$, the energy barriers of M mode are smaller than that of S mode. The energy barriers of M mode are larger than that of S mode for $18R_1 \rightarrow 18R_2$ and $14H_2 \rightarrow 14H_5$. It is found that the energy barriers increase with the increasing of the numbers of AA stacking of the different slip modes.



## 1. Introduction

Magnesium alloys containing rare-earth (RE) elements have be considerably concerned in the recent years due to their unique microstructure that could achieve high strength and excellent creep resistance. In the experimental aspect, the nanocrystalline rapid solidification powder metallurgy (RSP/M) alloy exhibited excellent tensile strength, however the ductility was very poor in the practical application [1,2]. Afterwards, it has been reported that $Mg_{97}$–$Zn_1$–$Y_2$ alloy would be a high strength magnesium alloy with good enough ductility. Particularly, the tensile yield strength and the elongation of the $Mg_{97}$–$Zn_1$–$Y_2$ alloy can respectively reach 600 MPa and 5% [3,4]. These excellent mechanical properties were derived from the combination of fine grain size, dispersion of fine particles and novel long-period stacking order (LPSO) structures [4].

The previous study [5] shows that the LPSO structures have the medium-range and the short-range ordering structure in each stacking fault as well as the long-range ordering one. To date, there have been reported about five kinds of LPSO structures by various experimental techniques in $Mg_{97}$–$Zn_1$–$Y_2$ alloy [6–13], such as 6H, 10H, 14H, 18R and 24R. And there are two types of microstructure for 6H, which are noted by $6H_1$: ABCBCB and $6H_2$: ABACAB. The 14H phases have five kinds of microstructures, which are noted by $14H_1$, $14H_2$, $14H_3$, $14H_4$ and $14H_5$, with stacking sequences ACBCBABABABCBC [6], ABABABACBCBCBC [7], ABABABACACACAC [8], ABACBCBCBCABAB [14] and ABABACBCBCBCAB [11]. For 18R phase, there are two types of microstructure denoted by $18R_1$: ACBCBCBACACACBABAB [12] and $18R_2$: ABABABCACACABCBCBC [6] respectively. It was reported that the 10H and 24R structure would have only one ordered hexagonal structure respectively [6], and their stacking sequences of the close-packed planes could be written as ABACBCBCAB and ABABABABCACACACABCBCBCBC. Compared with the perfect hexagonal close-packed (hcp) stacking sequence of close-packed planes, the LPSO phases in the Mg–Y–Zn alloys are actually multi-stacking fault structures (MSFSs) which consist of the basal stacking faults (SFs) [15,16]. Interestingly, many experimental observations [7,8] revealed that the inter-transformation would occur between LPSO phases. It was reported that $18R_1$ would transform into $14H_2$ by annealing at 773 K for 5 h [8] and $14H_3$ would transform into $6H_2$ by annealing at 573 K for 3.6 ks [7]. The transformation pathway of the $18R \rightarrow 14H$ was reported by Kiguchi et al. [5,17–23] and the appropriate heat treatments was necessary at 773 K for several hours in the Ar atmosphere and the 24R structure played a role in this transformation process.

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**Table 1**
Stacking sequence, SF energies and SF energy per fault of 6H, 10H, 14H, 18R and 24R v-LPSO Mg. The values in parentheses calculated with vacuum space. The unit of energy is mJ/m$^2$.

| System | Stacking sequences | SFs | Stacking fault energies(mJ/m$^2$) | |
|---|---|---|---|---|
| | | | This work | Cal. [15] |
| 6H | ABCBCB (1) | $2I_1$ | 43.37(35.34) | 44.08 |
| | | Per fault | 21.68(17.67) | 22.04 |
| | ABACAB (2) | $2I_1$ | 43.37(63.99) | 44.08 |
| | | Per fault | 21.68(31.99) | 22.04 |
| 10H | ABACBCBCAB | $2I_2$ | 76.62(97.98) | 64.96 |
| | | Per fault | 38.31(48.99) | 32.48 |
| | ACBCBABABABCBC (1) | $4I_1$ | 71.07(62.99) | 69.08 |
| | | Per fault | 17.77(15.75) | 17.27 |
| | ABABABACBCBCBC (2) | $2I_2$ | 60.43(35.69) | 63.32 |
| | | Per fault | 30.22(17.85) | 31.66 |
| 14H | ABABABACACACAC (3) | $2I_1$ | 34.15(19.83) | 33.06 |
| | | Per fault | 17.08(9.915) | 16.53 |
| | ABACBCBCBCABAB (4) | $2I_2$ | 60.44(74.58) | 63.32 |
| | | Per fault | 30.22(37.29) | 31.66 |
| | ABABACBCBCBCAB (5) | $2I_2$ | 60.44(88.31) | 63.32 |
| | | Per fault | 30.22(44.16) | 31.66 |
| 18R | ACBCBCBACACACBABAB(1) | $3I_2$ | 89.66(100.47) | 94.02 |
| | | Per fault | 29.89(33.49) | 31.34 |
| | ABABABCACACABCBCBC (2) | $3I_2$ | 89.66(70.03) | 94.02 |
| | | Per fault | 29.89(23.34) | 31.34 |
| 24R | ABABABABCACACACABCBCBCBC | $3I_2$ | 108.01(74.23) | 101.61 |
| | | Per fault | 36.0(24.74) | 33.87 |

In addition, the study [15] which focused on discussing first-principles calculations based on the density functional theory (DFT) reported that the MSFSs in pure Mg would be similar to the LPSO structures of Mg–Y–Zn alloy. After carefully observing on the stacking sequences of the LPSO phases in the close-packed planes, the five kinds of LPSO structures in pure Mg could be classified into two groups (I1-containing MSFSs and I2-containing MSFSs). In other words, all of these LPSO-like MSFSs mainly consist of $I_1$ and $I_2$ planar fault and each kind of structure would only have one type of SF. And they have been investigated systematically from first-principles calculations [15,16]. More importantly, the report [15] indicates that inter-transformation mainly occurs among LPSO structures with the same type of stacking faults when their lower stacking fault energies are closer. At the same time, it also mentioned that the SF energy differences would further decrease with the addition of Y and Zn atoms and the inter-transformation would become easier.

Based on the discussion above, our interest would be provoked for systematically investigating the transformation pathways among the LPSO phases in pure Mg. Although the previous study mentioned above has reported the inter-transformation between LPSO for pure Mg and the rule to achieve the phase transformation easily, the specific transformation pathways have not been investigated in theory. Therefore, based on first-principle calculations for generalized stacking fault (GSF) energy, the specific transformation pathways have been investigated systematically in this work. We also make the pathway optimization analysis by comparing the energy barriers for the transformation mechanisms containing multiple potential transformation pathways. In order to find the potential transformation pathways for the transformation mechanisms, two kinds of slip modes are proposed. One is the single-slip-plane mode (S mode). There is only one slip plane in each slip process and the transformations are obtained by several slip processes. The other is the multi-slip-planes mode (M mode). There are several slip planes in each slip process and the transformations can also be obtained by different slip processes. This should be helpful for further investigations and understanding the phase transformation of LPSO structures.

## 2. Computational method

In this study, first-principles study based on the DFT [24] is used to investigate the GSF energies of v-LPSO Mg and the calculations are performed by using the VASP code. The effects of exchange–correlation function are described with the generalized gradient approximation (GGA) [25,26] of Perdew–Burke–Eruzerhof (PBE) [27,28]. A plane-wave basis set is employed within the framework of the full potential frozen-core projector augmented wave (PAW) [29,30]. In order to get accurate results, the cut-off energy of plane wave is chosen at 500 eV. During the process of computation for the intrinsic stacking faults, the periodic supercells for the v-LPSO Mg were adopted as follows: $1 \times 1$ unit cells with 6 layers for 6H, 10 layers for 10H, 14 layers for 14H, 18 layers for 18R and 24 layers for 24R, respectively. When we calculate the GSF energies, the effects with and without vacuum space are also discussed and the thickness of vacuum space is set to 15 Å. For 2H–Mg, Brillouin-zone integrations are optimized by using the special *k*-point sampling of Monkhorst–Pack scheme [31] with a $21 \times 21 \times 21$ grid *k*-point Monkhorst–Pack scheme for the lattice constant calculation. In addition, for the calculations of the GSF energy, the *k*-point Monkhorst–Pack are set at $21 \times 21 \times 5$ for 6H and 10H. When the number of atomic layers contained in calculation supercell would be greater than 14, the *k*-point Monkhorst–Pack would be set at $21 \times 21 \times 1$. The relaxation of all internal atomic positions, unit cell volumes and shapes would not be considered during the whole calculation.

During the computational process for the GSF energies, we choose the least common multiple of the number of layers between the two transferable phases to establish the calculational supercell [32]. For example, we adopt $1 \times 1$ unit cells with 18 layers for the transformation between 6H and 18R, 24 layers for 6H and 24R, etc. For the perfect hcp stacking sequence of close-packed planes, the slip would be achieved easily along $[10\bar{1}0]$ direction, and the calculated value of GSF energies is still lower than others [33,34]. So we employ a slab to calculate the GSF energies of the transformation pathways, and the slip plane would be performed along $[10\bar{1}0]$ direction in $\{0001\}$ plane.