First-principles Investigations of Local Structures of LPSO Phases in Mg-TM-RE Alloys

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Mg alloys containing a small amount of TM (Transition Metal) and RE (Rare Earth) reveal excellent mechanical properties with high yield strength ~500 MPa and elongation ~5 % at room temperature. One of the remarkable microstructural features is formation of a novel type of long-period stacking/ordered (LPSO) structures [1]. They are unique structures, as being long-period chemical-ordered as well as stacking-ordered; their long-period stacking polytypes are denoted as 18R, 14H, 10H, 24R, all of which are composed of a common structural unit represented by local ABCA stacking where these 4 layers are significantly enriched by TM and RE [2]. Recently, based on Z-contrast STEM observations, we proposed structural models of LPSO phases [3]. In the proposed models, the characteristic ordered features of LPSO phases are represented by local TM_6RE_8 clusters, which are embedded in the local ABCA layers in accordance with the $L1_2$ type short range order.

Formations of TM_6RE_8 clusters in LPSO phases were confirmed in several Mg-TM-RE systems. Observed structures of TM_6RE_8 clusters, however, were slightly different on alloy systems. Therefore we also investigated differences of local structures in LPSO phases with first-principles calculations (VASP). In the system of Mg-Al-Gd, optimized LPSO structures do not reveal obvious relaxation and almost atoms reveal no significant displacement from the original hexagonal or rhombohedral sites. On the other hand, in the system of Mg-Zn-Y, optimized structures revealed significant displacements of Zn and Y atoms. The significant relaxations in the Mg-Zn-Y system suggest a possible other local structures of Zn_6Y_8 clusters. In the present work, we investigate possibilities of other local structures in the LPSO phases with first-principles calculations.

The model structure used in this work is 14H-LPSO structure composed of $Mg_{140}TM_{12}RE_{16}$. Fig. 1 shows optimized local structures around the TM_6RE_8 clusters in the LPSO structures of (a): $Mg_{140}Al_{12}Gd_{16}$ and (b): $Mg_{140}Zn_{12}Y_{16}$, whose lattice parameters were slightly expanded from the ones of initial structure. The conditions for calculations are denoted in the caption. Looking carefully the optimized structures in Mg-Zn-Y system, we found that significant displacements of Zn/Y atoms cause formation of internal voids at the center of clusters, which are capable for placing one extra atom. Then, introducing another atom to each relaxed Zn_6Y_8 cluster, we constructed new structural models, which is composed of $Mg_{140}Zn_{12}Y_{16}X_2$ (X = Mg/Zn/Y). From the calculation, $Mg_{140}Zn_{12}Y_{16}X_2$ structures revealed higher stabilities than the $Mg_{140}Zn_{12}Y_{16}$ structure, regardless of elements X. For investigating occurrences of the $Mg_{140}Zn_{12}Y_{16}X_2$ structures in LPSO phases, we performed direct observations of the LPSO phases in Mg-Zn-Y system by HAADF/ABF-STEM. Fig. 2 shows HAADF/ABF-STEM images of LPSO phases, obtained along $[1\bar{1}00]$ directions. The red-frame areas in the images correspond to Zn-Y clusters. As the intensities at the center of clusters in image (a) are weaker than the ones of Zn/Y columns, we consider

that the element X is not Zn and/or Y. Investigating ABF-STEM images with simulations; we are able to evaluate the possibility that Mg atoms occupy the center of clusters.

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References
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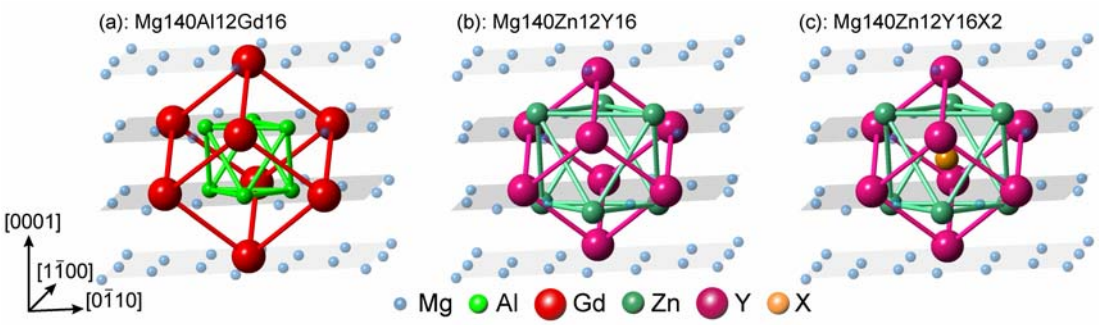

Fig. 1. Local optimized structures around TM-RE clusters embedded in ABCA layers in LPSO; (a) $Mg_{140}Al_{12}Gd_{16}$, (b)$Mg_{140}Zn_{12}Y_{16}$, (c)$Mg_{140}Zn_{12}Y_{16}X_2$. For calculations, we chose the conditions as follows: cut off energy = 340 eV, convergence = 1.00E-005 eV, algorithm = Normal (blocked Davidson), k-mesh = 3x3x1. Lattice parameters of (a) and (b) are almost equal; a = 1.12, c = 3.63 nm, which are slightly expanded from the initial structure (a =1.11, c = 3.61 nm).

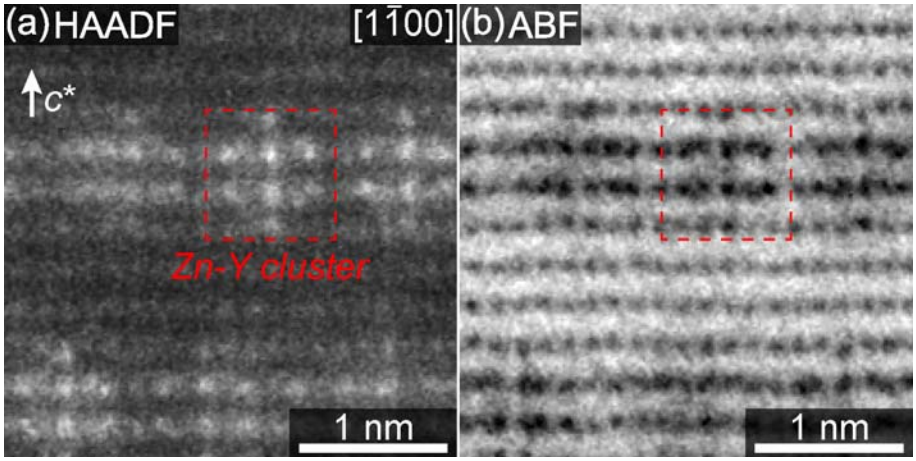

Fig. 2. (a): HAADF and (b): ABF-STEM images of the LPSO phases in $Mg_{85}Zn_6Y_9$ (at. %) alloys, obtained along [1$\bar{1}$00] directions by Cs-corrected STEM.