Detailed Structures and Formation Mechanisms of Well-Known $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ Phase in Die-Cast $\text{Mg}-4\text{Al}-4\text{RE}-0.3\text{Mn}$ Alloy

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Abstract

The detailed structures and the corresponding formation mechanisms of the well-known $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase in the conventional die-cast $\text{Mg}-4\text{Al}-4\text{RE}-0.3\text{Mn}$ alloy were thoroughly investigated using transmission electron microscopy (TEM). The results indicate that the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase ordinarily contains both normal $(11\bar{2}1)$ twins and orientation twins. Both detailed TEM observations and density functional theory calculations indicate that the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is transferred from the $\text{Al}_8\text{RE}\text{Mn}_4$ phase following an orientation relationship as $[010]_{\text{Al}_8\text{RE}\text{Mn}_4} // [\bar{1}101]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ and $(101)_{\text{Al}_8\text{RE}\text{Mn}_4} // (11\bar{2}0)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$. Moreover, forming orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is attributed to the blurry regions at incoherent twin boundaries in the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. Finally, these formed orientation twins result in the $(11\bar{2}1)$ twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase.

Keywords Transmission electron microscopy · Phase transformation · Intermetallic phase · Twin boundary · Orientation relationship

1 Introduction

High-pressure die-cast (HPDC) $\text{Mg}-\text{Al}-\text{RE}$ -based alloys have been receiving the greatest interest in applying to powertrain components in automobile and aerospace industries due to their outstanding high-temperature performance [1–8]. For improving corrosion resistance,

manganese primarily considered as an iron remover is ordinarily added into $\text{Mg}-\text{Al}-\text{RE}$ -based magnesium alloys [9, 10]. Inevitably, some Mn-containing intermetallic phases would form during solidification or the following heat treatments. These Mn-containing intermetallic phases have various influences on alloys' both microstructures and performance [11–16]. For example, Danaie et al. [11] reported that the Al–Mn intermetallics such as Al_8Mn_5 are cathodic with respect to the α -Mg matrix. Furthermore, Wang et al. [12] and Laser et al. [13] pointed out that both β -Mn(Al) and Al_8Mn_5 particles can primarily crystallize during the solidification in the Mn-contained $\text{Mg}-\text{Al}-\text{Zn}$ -based alloys and may act as potential heterogeneous nucleation sites for Mg grains, thus being potential grain refiners. With respect to mechanical properties, Homma et al. [14] and Zhu et al. [15] stated that the Mn addition can obviously improve the alloys' creep resistance. Furthermore, Zhu et al. [16] also reported that the minor Mn addition could significantly enhance the age hardenability of the die-cast $\text{Mg}-\text{Al}-\text{RE}$ alloys. However, the Mn-containing particles are often with relatively too large volume in the conventional die-cast $\text{Mg}-\text{Al}-\text{RE}$ -based alloys such as AE42 ($\text{Mg}-4\text{Al}-2\text{RE}-0.3\text{Mn}$, wt%) and AE44 ($\text{Mg}-4\text{Al}-4\text{RE}-0.3\text{Mn}$, wt%) [17–19]. For instance, Pettersen

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et al. [19] reported that the lumpy Mn-containing particles are with size of 0.5–4 μm . Subsequently, these large intermetallic particles lead to a negative effect on the alloys' mechanical properties [17]. Generally, the typical large Mn-containing phase in the conventional die-cast Mg–Al–RE-based alloys is $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ ($R\bar{3}m$ space group, lattice parameters $a = 0.904$ nm, $c = 1.317$ nm [20]). It ordinarily locates on grain boundaries, and owns either hexagonal or lumpy morphology. In addition, it has relatively large volume [19, 21, 22]. Therefore, it is of vital importance to refine its morphology for decreasing its negative effects on alloys' performance. It is well known that one outstanding prerequisite in designing and understanding how to control phase morphology is to accurately identify the structural characteristics and possible formation mechanisms [10]. In 1996, Pettersen et al. [19] pointed out that the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is often as polycrystals. Nevertheless, the corresponding detailed structures and formation mechanisms have been hitherto scarcely investigated. Herein, the emphasis of this work is thus on revealing the detailed structures and the underlying formation mechanisms of the well-known $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase in the die-cast AE44 alloys using TEM.

2 Experimental and First-Principles Calculation Details

The AE44 (RE = Ce and La) alloy was prepared from high-purity magnesium and aluminum, Mg–20 wt% RE and Mg–2 wt% Mn master alloys. The alloy melt was produced in a resistance-heated crucible under the protection of continuously flushed $\text{CO}_2 + 1$ vol% SF_6 mixed gas. Then, the melt was held at approximately 710 °C and finally was cast using a 280-ton clamping force cold chamber die-cast machine. The chemical compositions of the obtained samples were determined by inductivity coupled plasma atomic emission spectroscopy (ICP-AES) apparatus and are Mg–3.73Al–1.97Ce–1.76La–0.27Mn (wt%). The microstructures were characterized using FEI Tecnai G² F20 TEM at 200 kV equipped with an energy-dispersive spectrometer (EDS). TEM foils in the form of 3-mm-diameter disks were mechanically grounded to approximately 30 μm and then ion-milled by a precision ion polishing system (PIPS Gatan) equipped with cooling system by liquid nitrogen. In order to intuitively see the difference of the distribution of alloying elements, the intensity values of the EDS mappings were displayed in two-dimensional (2D) graphs via MATLAB.

First-principles density functional theory (DFT) calculations in this work were carried out at 0 K, employing the Vienna ab initio Simulation Package (VASP 5.2.2) [23].

The exchange and correlation interactions were described using projector-augmented plane wave (PAW) of the generalized gradient approximation [24, 25]. The cutoff energy was set to be 400 eV, with k -point meshes of $10 \times 10 \times 10$ for both $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 , respectively. For simplification, RE is represented by Ce in all DFT calculations. Firstly, the total energy as a functional of volume is calculated and fitted by the Birch–Murnaghan equation of state (see elsewhere) [26, 27]. Then, the structures at their equilibrium volumes were fully relaxed. Finally, the calculated lattice parameters were obtained and the formation enthalpies (ΔH) were calculated as follows:

$$\Delta H = (E_{\text{total}} - AE_{\text{Al}} - BE_{\text{Ce}} - CE_{\text{Mn}})/(A + B + C), \quad (1)$$

where E_{total} is the total energy of $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ or Al_8REMn_4 , E_{Al} , E_{Ce} and E_{Mn} are the total energies per atom of Al, Ce and Mn, respectively, at their ground-state structures, and A , B and C are the numbers of Al, Ce and Mn atoms, respectively, in $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ or Al_8REMn_4 .

3 Results and Discussion

Figure 1a shows the bright-field (BF) TEM image of a typical Mn-containing particle in the studied alloy. This particle is with a size of approximately 1.5 μm and is often consisted of several radial blocky segments. This phenomenon is very similar to that reported for the Al_8Mn_5 phase in Ref. [28]. Based on the corresponding selected area electron diffraction (SAED) patterns (Fig. 1b, c), both segments are the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase, but with no identical orientation relationship between them. In addition, Fig. 1c indicates that there are some twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. Since the $(11\bar{2}1)$ plane serves as the twinning plane, the twins were defined as $(11\bar{2}1)$ twins. In addition, there are also some extra diffraction spots (indicated by green arrows) except those from the $(11\bar{2}1)$ twin domains (Fig. 1c). According to the measured corresponding inter-planar spacing, these extra diffraction spots would be from another type of domain with the axis being close to $[11\bar{2}0]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$. Although the approximately identical phenomenon has also been reported in our previous work [21], the underlying causes were not revealed. According to Ref. [21], each radial segment consists of many narrow and parallel strips, and two kinds of boundaries were found, namely $(11\bar{2}1)$ twin boundary (TB) and orientation twin (orientation domain) [29] (see Fig. 2d–f in Ref. [21]). However, the intersection angle between $[1\bar{5}43]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ and $[11\bar{2}0]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ (approximately 61.8°) is slightly deviated from the rotation angle for three or sixfold symmetry operation (60° or 120°, respectively). This results in a total deviation of approximately 10.8° when $(11\bar{2}1)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$

Fig. 1 **a** BF-TEM image of a typical lumpy particle, corresponding SAED patterns of **b** B segment, **c** C segment, respectively. The corresponding planar spacings for $(h_1k_1i_1l_1)$ and $(h_2k_2i_2l_2)$ diffraction spots are shown in **c**

Fig. 2 BF-TEM image of representative interlaced lath-shaped particles, with the inset being the magnified image of region highlighted by a purple quadrate

plane matches the $(0001)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane. It is calculated that $d_{(0001)} = 1.317 \text{ nm}$ and $d_{(11\bar{2}1)} = 0.428 \text{ nm}$. Furthermore, Fig. 1c illustrates that $d_{(0001)} = 3d_{(11\bar{2}1)}$. The mismatches are approximately 3.8% and 2.0% with and without a 10.8° deviation, respectively. Therefore, the axis deviation of the orientation twin decreases the strain energy. This is well in line with Ref. [21]. Based on TEM observations, most $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ particles simultaneously contain normal $(11\bar{2}1)$ twins and orientation twins. This unusual structure was not reported anywhere and possibly corresponds to its especial formation mechanism. In the following, we will reveal it using TEM observations and DFT calculations.

Figure 2 shows a representative BF-TEM image of an interlaced lath-shaped Al-RE-Mn phase. Similar to the

aforementioned lumpy particle, this particle is also composed of several lath-shaped segments (labeled by 1–5), and there is no identical orientation relationship between any two adjacent ones. This phase was also reported in our previous work [21], but only one part was characterized. In this work, another part labeled as 2 and shown in the inset of Fig. 2 was also characterized in detail. It can be seen that most of the lath-shaped segments simultaneously contain two coexisted parallel components. To identify their crystal structures, SAED patterns from local regions are presented in Fig. 3. The results clearly indicate that the two particles labeled as 1 and 2 simultaneously contain two Al-RE-Mn phases: Al_8REMn_4 (tetragonal structure, $a = 0.898 \text{ nm}$ and $c = 0.517 \text{ nm}$ [28]) and $\text{Al}_{10}\text{RE}_2\text{Mn}_7$. In addition, there are also some twins in the Al_8REMn_4 phase (Fig. 3a). Since the (101) plane serves as the twinning plane, the twins in the Al_8REMn_4 phase are (101) twins. Furthermore, no clear extra diffraction spots are observed in Fig. 3a. This suggests that there would be no orientation twin in the Al_8REMn_4 phase. Figure 3b presents the SAED pattern from region B, which was taken with same tilting angles as those for Fig. 3a. The results suggest that these two intermetallic phases stand following a certain orientation relationship, which can be seen more intuitively from Fig. 3c. The $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is simultaneously coherent with both the matrix and twins of the Al_8REMn_4 phase. The orientation relationship between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 is as $[010]_{\text{Al}_8\text{REMn}_4} // [\bar{1}101]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ and $(101)_{\text{Al}_8\text{REMn}_4} // (11\bar{2}0)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$. Figure 3d and e presents the SAED patterns for the lanky lath-shaped phase and the attached convex phase, respectively. The results demonstrate that the former one is $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and the latter one is Al_8REMn_4 . In addition, both of them contain twins, and the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase also contains orientation twins. However, the $[1\bar{5}43]$ axis of the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is not parallel to the $[1\bar{1}1]$ axis of the Al_8REMn_4 phase. To confirm whether these two phases still follow a same

Fig. 3 SAED patterns from local regions indicated by area A **a**, area B **b**, area C **c**, area D **d**, area E **e**, area F **f** in Fig. 2

orientation relationship as the above mentioned, Fig. 2f shows the SAED pattern from the phase boundary region (labeled by F). The Al_8REMn_4 phase is simultaneously coherent with both matrix and twins of the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. In addition, the orientation relationship between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 is fully consistent with the above mentioned. Figure 4a shows the high-angle annular dark-field scanning TEM (HAADF-STEM) image of the interlaced lath-shaped Al–RE–Mn phase shown in Fig. 2. The corresponding EDS mappings of Al, La, Ce and Mn for the region denoted by a yellow box are shown in

Fig. 4b. The results demonstrate that A and E phases contain slightly higher Al content than B and D phases, but B and D phases contain slightly higher RE content than A and E phases. The contrast of Mn atoms cannot be clearly discerned. The intensity values of Fig. 4b were further displayed in 2D graphs via MATLAB [30] (Fig. 4c). It certifies that RE atoms are proved to be enriched in B and D phases, while Al atoms in A and E phases. Furthermore, Mn atoms are proved to be slightly more enriched in B and D phases compared with those in A and E phases. According to their chemical formulae, the atomic contents

Fig. 4 **a** HAADF-STEM images of interlaced lath-shaped Al–RE–Mn phase, **b** EDS mappings of Al, La, Ce and Mn elements for region indicated by yellow dotted quadrangle in **a**, **c** 2D graphs via MATLAB of intensity values of Al, La, Ce and Mn elements in **b**, respectively

of Al, RE and Mn are approximately 0.526, 0.105 and 0.368, respectively, for the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase, and are approximately 0.615, 0.077 and 0.308, respectively, for the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. Thus, the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase contains slightly higher RE and Mn contents than the $\text{Al}_8\text{RE}\text{Mn}_4$ phase, while the $\text{Al}_8\text{RE}\text{Mn}_4$ phase contains higher Al content than the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. The intensity analysis on the corresponding EDS mappings further confirms that the A and E phases are $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and the B and D phases are $\text{Al}_8\text{RE}\text{Mn}_4$.

Figure 5a shows the magnified BF-TEM micrograph and the corresponding SAED pattern of the phase boundary between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and $\text{Al}_8\text{RE}\text{Mn}_4$. Obvious traces of phase boundary (highlighted by purple arrows) and some twin boundaries (TBs) (highlighted by green arrows) in the $\text{Al}_8\text{RE}\text{Mn}_4$ phase were observed. According to the corresponding HR-TEM observations (Fig. 5b, c), two types of TBs in the $\text{Al}_8\text{RE}\text{Mn}_4$ phase were revealed. One type of TB (Fig. 5b) is a common coherent TB (CTB) with the $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ plane serving as the twinning plane. The other one (Fig. 5c) is an incoherent twin boundaries (ITB) as marked by a green dotted line, and the twinning plane is parallel to $(110)_{\text{Al}_8\text{RE}\text{Mn}_4}$ of region D or $(011)_{\text{Al}_8\text{RE}\text{Mn}_4}$ of region C. Additionally, a blurry boundary as highlighted by a green dotted circle (labeled as E1) was always observed at the ITBs. Generally, the corresponding fast Fourier

transform (FFT) pattern from the ITB region such as the E2 region is the recombination of the FFT patterns from the bilateral twinned regions. However, the FFT pattern from the E1 region shows some extra diffraction spots (indicated by green circles). Furthermore, these extra diffraction spots indicate a maximum inter-planar spacing of ~ 0.896 nm, which is approximately twice to $d_{(101)}$ but highly identical to $d_{(100)}$ for the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. Therefore, these extra spots from the blurry region probably suggest the appearance of the $(100)_{\text{Al}_8\text{RE}\text{Mn}_4}$ plane. In other words, the blurry region at the ITB of $\text{Al}_8\text{RE}\text{Mn}_4$ phase is rotated from the twinned domains. Figure 5d shows the HR-TEM image of a triangle region between two twinned $\text{Al}_8\text{RE}\text{Mn}_4$ domains and an $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain. The $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is simultaneously coherent with the twinned $\text{Al}_8\text{RE}\text{Mn}_4$ domains, and the phase boundaries between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and $\text{Al}_8\text{RE}\text{Mn}_4$ can be classified into two types as labeled by I and II. The corresponding magnified HR-TEM images along with the FFT patterns of I- and II-type boundaries are illustrated in Fig. 5e, f, respectively. The results indicate that both I- and II-type boundaries are not straight but zigzag, with $(110)_{\text{Al}_8\text{RE}\text{Mn}_4}$ matching $(1\bar{2}13)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$, or with $(011)_{\text{Al}_8\text{RE}\text{Mn}_4}$ matching $(10\bar{1}1)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$. Also, these two boundaries can be regarded to be fully consistent. Furthermore, there is no structural change near the CTB.

Fig. 5 a BF-TEM image along with corresponding SAED pattern of segment 1 in Fig. 2a, b–f HR-TEM images along with corresponding FFT patterns from local regions. The orange dotted lines highlight the (110) plane, the absinth-green dotted lines highlight the CTB, the blue dotted lines schematically highlight the phase boundaries, the green dotted lines highlight the ITB, and the green dotted circles highlight the blurry region at the ITB

Therefore, the twins with CTBs in the Al_8REMn_4 phase cannot result in general twins or orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase if the Al_8REMn_4 phase would transfer to the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. Thus, the underlying cause to the formation of the orientation twin in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase will be analyzed from the ITBs in the Al_8REMn_4 phase or from its own fine structures.

Figure 6a shows some parallel twin strips in the lath-shaped $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. Some bands with different lattice fringes lie at the TBs as indicated by yellow arrows. From the corresponding SAED pattern and the HR-TEM image along with the FFT patterns from A–C regions (shown in Fig. 6b, c, respectively), the interlayer between two twinned $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domains was identified to be $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase, but with a different orientation from that of the twinned domains. Thus, these bands are orientation twins. This is highly identical with that in the lumpy particle as shown in Fig. 1. Both Figs. 1 and 6 suggest that

Fig. 6 **a** BF-TEM image of $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase in interlaced lath-shaped particle, **b** corresponding SAED pattern along with pattern intensity values along orange and purple dotted lines in SAED pattern, and **c** corresponding HR-TEM image along with FFT pattern, also with FFT patterns A–C from local regions of A–C, respectively, indicated by yellow quadrates in **c** (d : spacing of two adjacent diffraction spots as indicated by intensity peaks)

most of the orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase distribute at the traditional twin boundaries, although some of them seem to be embedded in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ matrix such as shown in Fig. 7. Then, is the formation of orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase due to the $(11\bar{2}1)$ twins? If yes, one $(11\bar{2}1)$ TB would be replaced by two orientation twin boundaries (OTBs) plus one $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain. The $(11\bar{2}1)$ plane of the matrix can perfectly match with the $(11\bar{2}1)$ plane of the twinned domain, while there is an approximately 2.0% mismatch when matching with the (0001) plane of the orientation twin domain. This indicates that forming an orientation twin in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase at its own TB will increase the strain energy, thus energetically unfavorable. Therefore, the orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase should not be formed at its own TB.

Ordinarily, the formation of a twin is closely related with the low-stacking fault energy of the investigated material [31]. In addition, forming a 60° or 120° orientation domain requires that the product phase must be transformed from a parent phase which belongs to a space group with higher symmetry and contains three or sixfold symmetry operations [29]. However, it is hard to determine which is the parent phase based on the crystal structures of $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 . In this work, DFT calculations were performed on the configurations of both $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 (Fig. 8) to estimate their relative stability. Table 1 presents the calculated lattice parameters, total energies and formation enthalpies for both $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 . The calculated lattice parameters reasonably agree with the experimental values [20, 28], which suggests that our calculations are reliable. With respect to the formation enthalpy, a negative value indicates a driving force toward the formation [32]. The

Fig. 7 HR-TEM image along with corresponding FFT patterns of an orientation twin in $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase. The bilateral $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domains of the orientation twin stand with fully consistent orientation

Fig. 8 Atomic configurations of $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 compounds

Table 1 Calculated lattice parameters, total energies and formation enthalpies for both $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 structures as shown in Fig. 8

Phase	Lattice parameter (nm)	E_{total} (eV)	ΔH (eV/atom)
$\text{Al}_{10}\text{RE}_2\text{Mn}_7$	$a = 0.874$, $c = 1.297$	− 346.656	− 2.165
Al_8REMn_4	$a = 0.889$, $c = 0.526$	− 150.168	− 1.898

calculated formation enthalpy values for $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and Al_8REMn_4 are − 2.165 and − 1.898 eV/atom, respectively. Therefore, the formation of both is energy favorable. However, formation enthalpy difference does not manifest the relative stability of the two given phases [32]. Recently, the relative stability of two compounds has been ordinarily determined by energy change of a phase transformation reaction [32]. Thus, we assumed that the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase would transfer to the Al_8REMn_4 phase:

Subsequently, the formation enthalpy for the transformation from $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ to Al_8REMn_4 was calculated to be 0.315 eV/atom. The positive value indicates that the transformation from $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ to Al_8REMn_4 is endothermic. Thus, the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase may be the product phase and could be transformed from the Al_8REMn_4 phase. There is no normative threefold or sixfold symmetry operation for Al_8REMn_4 . Therefore, the formation of orientation twin in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is not attributed to the lost of symmetry operations during phase transformation. Furthermore, the formation of orientation twin in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is also not attributed to the CTB in the Al_8REMn_4 phase and its own TB. Thus, the ITB in the Al_8REMn_4 phase (Fig. 5c) has to be considered in this work. According to its expansive image as shown in Fig. 9, although the corresponding TB is incoherent, the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is also simultaneously coherent with the twinned Al_8REMn_4 domains. Therefore, the ITB in the Al_8REMn_4 phase does also not result in orientation domain in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase during phase transformation. However, it should also be noted that there are always some blurry regions at the ITBs of the Al_8REMn_4 phase (Fig. 5c). As mentioned above, this blurry region results in some extra diffraction spots in the corresponding FFT pattern. These extra diffraction spots probably correspond to the $(100)_{\text{Al}_8\text{REMn}_4}$ plane. Thus, we regard that the blurry

Fig. 9 Expansive HR-TEM image of Fig. 5c and corresponding FFT patterns from local regions of C–F, where the purple dotted lines marked the trace of $(10\bar{1}1)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7} // (101)_{\text{Al}_8\text{REMn}_4}$. In addition, the part of the line in the region highlighted by green dotted circle was highlighted by white dotted line

region was formed by a rotation from $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ to $(100)_{\text{Al}_8\text{RE}\text{Mn}_4}$ around the $[010]_{\text{Al}_8\text{RE}\text{Mn}_4}$ axis. The corresponding rotation angle is approximately 60.1° . In addition, there is only one way for the phase transformation from $\text{Al}_8\text{RE}\text{Mn}_4$ to $\text{Al}_{10}\text{RE}_2\text{Mn}_7$. Thus, the $(11\bar{2}0)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane is parallel to the $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ plane during the whole transformation. When the phase transformation spreads to the blurry regions at ITBs, the $(10\bar{1}1)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane has to rotate around $[11\bar{2}0]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ by a same angle. This directly results in a small $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain with the $(10\bar{1}1)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane rotated around $[11\bar{2}0]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ by approximately 60.1° . Subsequently, the $[11\bar{2}0]$ axis of the small $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain is approximately parallel to the $[1\bar{5}43]$ axis of the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ matrix, with the deviation angle of about 1.7° . This is in full agreement with the SAED results shown in Figs. 1c and 6b. Thus, the formation of orientation twin in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is closely related to the blurry region at the ITBs in the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. When the phase boundary carries through the blurry region, the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase will meet with the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. At this moment, the $(11\bar{2}5)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane will match with the $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ plane. This matching mode deviates from the phase transformation way in which the $(11\bar{2}0)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ plane is parallel to the $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ plane. However, only one orientation relationship between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and $\text{Al}_8\text{RE}\text{Mn}_4$ was observed in this work. Therefore, the phase transformation will continue following the unique orientation relationship between $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ and $\text{Al}_8\text{RE}\text{Mn}_4$. Then, the later formed $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain has to stand with the small $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domain following $(11\bar{2}1)/(0001)$. However, there are two modes: One is that the bilateral $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domains of the small orientation twin stand fully consistently, and the other one is that the bilateral $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ domains of the small orientation twin are with indirect twin relationship. This is the underlying reason for that the orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase were observed both at TBs (Fig. 6a) and in matrix (Fig. 7). Therefore, the formation of normal $(11\bar{2}1)$ twins is closely related to the orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase.

4 Conclusion

The lumpy $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase often consisted of several radial blocky segments, and each segment contains normal $(11\bar{2}1)$ twins and orientation twins. In addition, the $\text{Al}_8\text{RE}\text{Mn}_4$ phase containing many twins and coexisting with $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase was also observed in the studied alloy. In this phase, some rotation regions with $(101)_{\text{Al}_8\text{RE}\text{Mn}_4}$ being

rotated to $(100)_{\text{Al}_8\text{RE}\text{Mn}_4}$ around $[010]_{\text{Al}_8\text{RE}\text{Mn}_4}$ by approximately 60.1° were observed at ITBs. Both detailed TEM observations and DFT calculations indicate that the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase was transferred from the $\text{Al}_8\text{RE}\text{Mn}_4$ phase following an orientation relationship as $[010]_{\text{Al}_8\text{RE}\text{Mn}_4} // [\bar{1}101]_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$ and $(101)_{\text{Al}_8\text{RE}\text{Mn}_4} // (11\bar{2}0)_{\text{Al}_{10}\text{RE}_2\text{Mn}_7}$. Moreover, forming orientation twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase is attributed to the blurry regions at ITBs in the $\text{Al}_8\text{RE}\text{Mn}_4$ phase. Finally, these formed orientation twins result in the $(11\bar{2}1)$ twins in the $\text{Al}_{10}\text{RE}_2\text{Mn}_7$ phase.

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