Formation and Relative Stabilities of Core-Shelled $L1_2$ -Phase Nano-structures in Dilute Al–Sc–Er Alloys

Chaomin Zhang^{1,2} · Yong Jiang² · Xiuhua Guo^{1,3,4} · Kexing Song^{1,3,5}

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Abstract

First-principles thermodynamic calculations were carried out at the interface level for understanding the precipitation of coherent $L1_2$ -phase nano-structures in dilute Al–Sc–Er alloys. All energetics, relevant to bulk substitution, interface formation, interfacial coherent strain and segregation, were calculated and used to evaluate the nucleation and relative stabilities of various possible $L1_2$ nano-structures. Only matrix-dissolved solute Er (or Sc) can substitute Sc (or Er) in $L1_2$ - Al_3Sc (or Al_3Er). The inter-substitution between $L1_2$ - Al_3Sc and Al_3Er is not energy feasible. Ternary $L1_2$ - $Al_3(Er_xSc_{1-x})$ precipitates tend to form the Al_3Er -core and Al_3Sc -shell structure with a sharp core/shell interface. Three possible formation mechanisms were proposed and examined. The effects of Er/Sc ratio and aging temperature on the relative stabilities of $L1_2$ -phase nano-structures in Al were also discussed.

Keywords Al–Sc–Er alloy · $L1_2$ phase · Core-shell · Interface · First-principles

1 Introduction

Micro-alloying with Sc in pure Al can cause a high-density precipitation of thermally stable, coherent $L1_2$ -phase Al_3Sc nanoparticles, leading to the largest strengthening effect per solute atom among all available alloying elements in

Al [1–3]. Although it is regarded as one of the most efficient solute elements, Sc is still too expensive for its large-scale applications in Al alloys. Also, the addition of Sc in Al is highly restricted by its very limited solubility. Seeking candidate elements for substituting Sc in Al alloys has thus attracted considerable attentions. Many transition metal [4–12] and rare-earth elements [13–16] have been experimentally tested and shown more or less promises in this respect. Among which, Er stands out for it has a similar eutectic reaction and a comparable atomic diffusivity in Al (of $4 \times 10^{-19} \text{ m}^2/\text{s}$ [17] versus the $0.9 \times 10^{-19} \text{ m}^2/\text{s}$ of Sc at 300 °C in Al [18]) as Sc does. The proper lattice misfit ($\sim 4\%$) between $L1_2$ - Al_3Er and Al is also favorable for strengthening the Al matrix [19]. Further studies showed that micro-alloying with both Sc and Er leads to the formation of ternary $L1_2$ - $Al_3(Sc_xEr_{1-x})$ nanoparticles after aging treatment, bringing about evident improvement in both the creep- and the coarsening-resistant properties of dilute Al–Sc–Er alloys up to 300–350 °C [14, 20]. This makes dilute Al–Sc–Er alloys promising for wide lightweight high-specific-strength structural applications in aerospace and automotive industries [1, 3]. The formation of ternary $L1_2$ - $Al_3(Sc_xEr_{1-x})$ in preference to binary $L1_2$ - Al_3Er and $L1_2$ - Al_3Sc in dilute Al–Sc–Er alloys has profound kinetic and thermodynamic origins and consequences.

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- ✉ Yong Jiang
yjiang@csu.edu.cn
- ✉ Kexing Song
kxsong@haust.edu.cn

- ¹ School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471023, People's Republic of China
- ² School of Materials Science and Engineering, Central South University, Changsha 410083, China
- ³ Henan Province Key Laboratory of Nonferrous Metal Material Science and Processing Technology, Luoyang 471023, People's Republic of China
- ⁴ Collaborative Innovation Center of Nonferrous Metals, Luoyang 471023, Henan Province, China
- ⁵ Provincial and Ministerial Co-construction of Collaborative Innovation Center for Non-ferrous Metal New Materials and Advanced Processing Technology, Luoyang 471023, Henan Province, People's Republic of China

Historically, the diffusion-controlling formation mechanism has been proposed [21] to explain the experimentally observed core-shell structure of $L1_2$ - $Al_3(Sc_xZr_{1-x})$ nano-precipitates in Al–Sc–Zr alloys. It was suggested that ternary $L1_2$ -phase nano-precipitates tend to form a Sc-rich core and Zr-rich shell structure (namely the $L1_2$ - $Al_3Zr(Sc)$ structure), as a direct consequence of the four-order-of-magnitude higher diffusivity of Sc than Zr in Al [17, 18]. Very recently, one our first-principles study indicated that the $L1_2$ - $Al_3Zr(Sc)$ structure is also the most energetically favored, although various other structures including the homogeneous random structure could coexist for extremely fine-sized nanoparticles ($R < \sim 1$ – 2 nm) [22]. However, in the case of Al–Sc–Er alloys, considering the fact that Er and Sc diffusivities are of the same order of magnitude (10^{-19} m²/s) at ~ 300 °C in pure Al, the diffusion-controlling mechanism would cause some uncertainty in predicting the core-shell structure for $L1_2$ - $Al_3(Er_xSc_{1-x})$. Would $L1_2$ - $Al_3(Er_xSc_{1-x})$ be still likely to form a core-shelled structure in Al–Sc–Er alloys? If so, which core-shelled structure would be more favored to form, the $L1_2$ - $Al_3Er(Sc)$ or the $L1_2$ - $Al_3Sc(Er)$ structure? Further experiment studies made the problems even more intriguing. It was found that the diffusivity of Er may decrease by three orders of magnitude when co-alloyed with Sc in Al [14]. If this occurs, owing to the largely retarded diffusion of Er, one of the two following consequences can be naturally deduced: (1) ternary $L1_2$ -phase nano-precipitates with an Er-rich shell and Sc-rich core structure, i.e., $L1_2$ - $Al_3Er(Sc)$, are more likely to form in Al–Sc–Er alloys, according to the diffusion-controlling mechanism, or (2) Er can hardly influence the kinetic diffusion of Sc and hence the precipitation of $L1_2$ - Al_3Sc , so that the separate precipitation of binary $L1_2$ - Al_3Sc and $L1_2$ - Al_3Er shall be expected.

Advanced experimental characterizations have been resorted to clarify the structure and performance of $L1_2$ - $Al_3(Er_xSc_{1-x})$. Three-dimensional atom-probe tomography (3D-APT) revealed that ternary $L1_2$ nano-precipitates in Al–Sc–Er alloys present the core-shelled structure of $L1_2$ - $Al_3Sc(Er)$ instead of $L1_2$ - $Al_3Er(Sc)$ [14]. This finding is somewhat surprising, for it is obviously against the prediction based on the diffusion-controlling mechanism. The totally different roles of Sc in forming ternary $L1_2$ nanoparticles in Al–Sc–Zr and Al–Sc–Er alloys become a puzzle: why and how can Sc, with a few orders-of-magnitude higher diffusivity in Al than both Zr and Er, be enriched in the core of $L1_2$ - $Al_3(Sc_xZr_{1-x})$ but in the shell of $L1_2$ - $Al_3(Sc_xEr_{1-x})$? Could the $L1_2$ - $Al_3Sc(Er)$ core-shell structure be also thermodynamically stable in Al–Sc–Er alloys, just as the $L1_2$ - $Al_3Zr(Sc)$ core-shell structure in Al–Sc–Zr alloys? For answers to these questions, a thorough assessment based on first-principles energetic calculations must be performed on all the relevant structures.

In this study, we performed the first-principles density functional theory (DFT) calculations to investigate the nucleation and structural stabilities of various possible $L1_2$ -phase nano-precipitates in dilute Al–Sc–Er alloys. Bulk substitution of elements was first evaluated among binary $L1_2$ - Al_3Er , Al_3Sc and the fcc-Al matrix. Interface modeling and calculations were then performed on the $Al_3Er(L1_2)/Al_3Sc(L1_2)$ interfaces. Based on the classic nucleation theory, all the interface and bulk results were then integrated to develop a fundamental understanding on the nucleation of various possible $L1_2$ nano-precipitates in Al–Sc–Er alloys, which enabled us to clarify the thermodynamic origin for the core-shelled structure of $L1_2$ - $Al_3Sc(Er)$ in dilute Al–Sc–Er alloys.

2 Computational methods

All first-principles calculations were conducted using the semi-commercial density functional theory (DFT) code–Vienna Ab-initio Simulation Package (VASP) [23, 24] based on the plane-wave basis sets and periodic boundary conditions. The ion–electron interactions were described by the Blöchl projector augmented wave method using the frozen-core approximation [25] as implemented in VASP. The Sc- $3s^23p^63d^14s^2$ electrons and Er- $5p^66s^24f^1$ electrons were treated as valence electrons. The pseudopotential generated within the generalized gradient approximation of Perdew–Burke–Ernzerhof [26, 27] was used for the exchange–correlation functionals. Based on a series of convergence tests, a Monkhorst–Pack K-mesh of $20 \times 20 \times 20$ (for Al_3Sc) and $15 \times 15 \times 15$ (for Al_3Er) were adopted for Brillouin zone integrations, and a high-energy cutoff of 400 eV was found to be sufficient. During structural relaxations, the electronic self-consistence loop was converged to 10^{-5} eV and atomic geometries were optimized until the Hellman–Feynman force on each ion was less than 0.01 eV/Å. By fitting the energy–volume results to the universal equation of state [28], the lattice constants (a) and bulk moduli (B) were calculated as $a = 4.040$ Å and $B = 77.9$ GPa for fcc-Al, $a = 4.106$ Å and $B = 86.7$ GPa for $L1_2$ - Al_3Sc , and $a = 4.232$ Å and $B = 78.1$ GPa for $L1_2$ - Al_3Er , respectively. All results were in good agreement with available experimental measurements [29–31] and other theoretical calculations [29, 32].

3 Results and Discussion

3.1 Solute substitution in $L1_2$ - Al_3Er and Al_3Sc

Previous experimental studies have suggested that Er has a high solubility up to 100% in $L1_2$ - Al_3Sc [33], but the

Sc solubility in L1₂-Al₃Er is still unknown. The actual composition of L1₂-Al₃(Sc_xEr_{1-x}) may vary largely with alloy chemistry and processing history. Apparently, the thermodynamics governing the formation of ternary L1₂ phases in Al-Sc-Er alloys through solute substitution must be first clarified. For this purpose, first-principles calculations were thus carried out to evaluate the Sc or Er substitution in binary L1₂-Al₃Er or Al₃Sc. Both the Al and X (X = Sc or Er) sublattices in L1₂-Al₃X can be considered as potential sites for substitution. All possible substitution pathways have been carefully examined. The substituting solute may come from either the Al matrix interior or the existing L1₂-Al₃X nano-phases, while the substituted atoms may enter into either the Al matrix or the existing L1₂-Al₃X nano-phases. The total energy difference before and after substitution defines the substitution energies per solute atom as

$$G_{\text{Er at Al}}^{\text{Al}_3\text{Sc}} = \left(G_{(\text{Al}_{80}\text{Er}_1)\text{Sc}_{27}}^{\text{tot}} + \mu_{\text{Al}} \right) - \left(G_{\text{Al}_{81}\text{Sc}_{27}}^{\text{tot}} + \mu_{\text{Er}} \right), \quad (1-a)$$

$$G_{\text{Er at Sc}}^{\text{Al}_3\text{Sc}} = \left(G_{\text{Al}_{81}(\text{Sc}_{26}\text{Er}_1)}^{\text{tot}} + \mu_{\text{Al}} \right) - \left(G_{\text{Al}_{81}\text{Sc}_{27}}^{\text{tot}} + \mu_{\text{Er}} \right), \quad (1-b)$$

$$G_{\text{Sc at Al}}^{\text{Al}_3\text{Er}} = \left(G_{(\text{Al}_{80}\text{Sc}_1)\text{Er}_{27}}^{\text{tot}} + \mu_{\text{Al}} \right) - \left(G_{\text{Al}_{81}\text{Er}_{27}}^{\text{tot}} + \mu_{\text{Sc}} \right), \quad (1-c)$$

$$G_{\text{Sc at Er}}^{\text{Al}_3\text{Er}} = \left(G_{\text{Al}_{81}(\text{Er}_{26}\text{Sc}_1)}^{\text{tot}} + \mu_{\text{Al}} \right) - \left(G_{\text{Al}_{81}\text{Er}_{27}}^{\text{tot}} + \mu_{\text{Sc}} \right), \quad (1-d)$$

where μ_i is the elemental chemical potential of i (= Al, Sc, or Er) in the L1₂-Al₃X phase or the fcc-Al matrix, depending on the choice of substitution pathway. Both the L1₂-Al₃X and the fcc-Al matrix were modeled using a 3 × 3 × 3 (108 atoms) supercell, i.e., $\mu_X = G_{\text{Al}_{107}\text{X}} - 107\mu_{\text{Al}}$, for a single X (= Er or Sc) in pure Al matrix and $\mu_X = (G_{\text{Al}_{81}\text{X}_{27}} - 81\mu_{\text{Al}})/27$ for a single X in L1₂-Al₃X. Due to large cancellation among the energy terms in Eq. (1), we ignored the entropy contribution

as the first-order approximation and evaluated the ΔG only in terms of enthalpy at 0 K. Such approximation was also adopted in Refs. [22, 32]. According to Eq. (1), a negative ΔG value predicts an energy favored substitution pathway.

The calculated substitution energies for all possible substitution pathways are summarized and compared in Table 1. It is obvious that both Er and Sc preferentially substitute for X in L1₂-Al₃X, in a way to favor the formation of ternary L1₂-Al₃(Er,Sc). This seems to be consistent with the experimental observations by 3D-APT [14]. The only feasible path for Sc substitution is that the matrix-dissolved Sc tends to substitute Er in L1₂-Al₃Er and the substituted Er stays in the L1₂-Al₃Er lattice, corresponding to a total energy reduction of 0.753 eV per Sc atom. The substitution path for Er was found similar. The matrix-dissolved Er tends to substitute Sc in L1₂-Al₃Sc, and the total energy can be reduced by 1.057 or 0.224 eV per Er atom, depending on the eventual destination of the substituted Sc atom. All other substitution pathways are energetically forbidden. We thus conclude that the formation of L1₂-Al₃(Sc_xEr_{1-x}) must involve the substitution of dissolved solute Sc (or Er) in binary L1₂-Al₃Er (or L1₂-Al₃Sc). The inter-substitution that is expected to occur between L1₂-Al₃Sc and Al₃Zr in the Al-Sc-Zr alloy system [22], and between L1₂-Al₃Er and Al₃Zr in the Al-Er-Zr alloy system [34], cannot possibly occur in the Al-Sc-Er alloy system from the viewpoint of thermodynamics.

3.2 Interface structures and energies: Al₃Er(L1₂)/Al₃Sc(L1₂)

Based on the cube-on-cube orientation relation [34], the Al/Al₃Er(L1₂) and Al/Al₃Sc(L1₂) interfaces have been intensively investigated from the first-principles in our previous studies [22, 35]. The Al₃Zr(L1₂)/Al₃Er(L1₂) interface, however, has never been theoretically studied in literatures. In this section, we adopted the same cube-on-cube orientation relation to construct the Al₃Sc/Al₃Er/Al₃Sc sandwich interface supercells with different contacting facets, namely the low-index {100},

Table 1 Calculated substitution energies (eV/atom) of Sc and Er in binary L1₂ phases

Substituting element	Substituted element	ΔE (eV/atom)	
		Substituted element goes into Al	Substituted element goes into Al ₃ X
Sc (in Al)	Al (in Al ₃ Er)	1.954	1.954
	Er (in Al ₃ Er)	0.038	-0.753
Sc (in Al ₃ Sc)	Al (in Al ₃ Er)	2.787	2.787
	Er (in Al ₃ Er)	1.212	0.081
Er (in Al)	Al (in Al ₃ Sc)	1.842	1.842
	Sc (in Al ₃ Sc)	-0.224	-1.057
Er (in Al ₃ Er)	Al (in Al ₃ Sc)	2.973	2.973
	Sc (in Al ₃ Sc)	0.908	0.074

{110} and {111} of Al_3X ($\text{X}=\text{Sc}, \text{Er}$). In each supercell, the Al_3Sc block includes 9 atomic layers of Sc and the Al_3Er block includes 5 to 7 atomic layers of Er, depending on the interface termination type. Considering the relatively lower bulk modulus of $\text{L1}_2\text{-Al}_3\text{Er}$ than $\text{L1}_2\text{-Al}_3\text{Sc}$, the Al_3Er lattice was stretched by $\sim 3.0\%$ to match the unstrained Al_3Sc into commensuration. Please note that the $\text{Al}_3\text{X}\{111\}$ is always terminated by the Al_3X layer, while the $\text{Al}_3\text{X}\{100\}$ and $\{110\}$ surfaces have an alternatively stacking structure of AlX and Al layers, and thus, each involves two possible termination types. For each termination, we further considered different interfacial coordination types, i.e., the top-, the bridge- and the hollow-coordinated, by translating the Al_3Sc lattice differently relative to the Al_3Er . A total number of ten interface ensembles were eventually constructed for energetics evaluation. Figure 1 shows the most energy-preferred interface structures after structural relaxation, namely the Al-terminated and bridge-coordinated interface of $(100)_{\text{Al}_3\text{Sc}}/(100)_{\text{Al}_3\text{Er}}$, the Al-terminated and hollow-coordinated interface of $(110)_{\text{Al}_3\text{Sc}}/(110)_{\text{Al}_3\text{Er}}$, and the AlEr-terminated and hollow-coordinated interface of $(111)_{\text{Al}_3\text{Sc}}/(111)_{\text{Al}_3\text{Er}}$. For clarity, only two interfacial layers are shown in the top views, where the smaller balls denote the atoms of the upper-layer right above and the bigger balls denote the atoms of the lower-layer right under the interface.

Following the procedure suggested by Refs. [36–38], the total energy change due to the interface formation between Al_3Sc or Al_3Er (ΔG_f) can be related to interface energy (γ) and interfacial coherent strain energy (G_{CS}) as

$$\frac{G_f}{N} = \frac{A}{N}\gamma + G_{\text{CS}}, \quad (2)$$

where A is the interface area and N is total atom number of interface supercell. By fitting the calculated $\Delta G_f/N$ versus $2A/N$ data into the linear relation in Eq. (2), one can deduce the coherent strain energy (ΔG_{CS}) and interface energy (γ) from the intercept and slope, respectively. This procedure was performed for $\text{Al}_3\text{Er}(\text{L1}_2)/\text{Al}_3\text{Sc}(\text{L1}_2)$ with the three different contacting facets as shown in Fig. 2. Clearly, the calculated interface energies are nearly zero for all the three different facets, indicating that such a hetero-interface can form very easily, and once forms, it can be very sharp. The nearly zero interface energy is also in coincidence with our earlier bulk calculations in Table 1 where the inter-substitution between $\text{L1}_2\text{-Al}_3\text{Sc}$ and $\text{L1}_2\text{-Al}_3\text{Er}$ bulks was predicted as thermodynamically forbidden.

3.3 Nucleation and structural stabilities of L1_2 nano-phases

It has been previously predicted that the $\text{Al}/\text{Al}_3\text{Er}(\text{L1}_2)$ and $\text{Al}/\text{Al}_3\text{Sc}(\text{L1}_2)$ interfaces have the lowest interface energy of 0.183 J/m^2 [35] and 0.164 J/m^2 [22], respectively. During bulk calculations in Sect. 3.1, we also obtained the bulk energies of -17.465 eV and -19.384 eV for $\text{Al}_3\text{Er}(\text{L1}_2)$ and $\text{Al}_3\text{Sc}(\text{L1}_2)$ per unit cell, respectively. All these interface and bulk energies are available for the theoretical assessment of nucleation and structural stabilities of all possible L1_2 nano-phases in Al-Sc-Er alloys. These nano-phases include the separately formed binary $\text{L1}_2\text{-Al}_3\text{Er}$ and $\text{L1}_2\text{-Al}_3\text{Sc}$, the homogeneous random structure of $\text{L1}_2\text{-Al}_3(\text{Sc}_x\text{Er}_{1-x})$, and the two core-shelled structures of $\text{L1}_2\text{-Al}_3\text{Er}(\text{Sc})$ and $\text{L1}_2\text{-Al}_3\text{Sc}(\text{Er})$. We note here that for the inner $\text{Al}_3\text{Er}/\text{Al}_3\text{Sc}$

Fig. 1 Energy-optimized $\text{Al}_3\text{Sc}(\text{L1}_2)/\text{Al}_3\text{Er}(\text{L1}_2)$ interface structures: **a** Al-terminated and bridge-coordinated $(100)_{\text{Al}_3\text{Sc}}/(100)_{\text{Al}_3\text{Er}}$ interface, **b** Al-terminated and hollow-coordinated $(110)_{\text{Al}_3\text{Sc}}/(110)_{\text{Al}_3\text{Er}}$ interface, **c** AlEr-terminated and hollow-coordinated $(111)_{\text{Al}_3\text{Sc}}/(111)_{\text{Al}_3\text{Er}}$ interface. Blue, green and orange balls represent Al, Sc and Er atoms, respectively. The red dash lines are used to locate the interfaces

Fig. 2 Predicted interface energy γ (J/m^2) and interfacial coherent strain energy ΔG_{CS} (eV/atom) for the $\text{Al}_3\text{Er}(\text{L1}_2)/\text{Al}_3\text{Sc}(\text{L1}_2)$ interfaces with various contacting facets of $(001)/(001)$, $(110)/(110)$ and $(111)/(111)$

interface in the two core-shell cases, the interface energies of the three facets (111)/(111), (110)/(110) and (100)/(100) are all very small and very comparable (Fig. 2). Such an energy isotropy would favor the formation of ball-shaped inner interface inside the core-shelled Al₃(Sc,Er) nanoparticles. The overall shape of Al₃(Sc,Er) nanoparticles is totally determined by the outer interface of Al/Al₃Sc or Al/Al₃Er. Thus, for stability evaluation of various nucleation structures, our calculations on Al/Al₃Sc or Al/Al₃Er adopted the (100)/(100) facet based on the minimal interface energy criterion. The minimal interface energy criterion is generally reasonable for describing a nucleation process.

3.3.1 Critical works of nucleation and nucleation radii

According to the classical nucleation theory, we assume a spherical shape L₁₂-phase nanoparticle with a radius R precipitating from the Al matrix. The total energy change owing to homogeneous nucleation is resulted from two competing energy contributions: the energy gain from the iso-volumetric substitution of the Al matrix with the L₁₂ nanoparticle ($=V \cdot \Delta \tilde{G}_V$) and the energy cost for creating the newborn interface area between the Al matrix and the L₁₂ nanoparticle ($=S \cdot \gamma$), i.e., $\Delta G = \frac{4\pi}{3} R^3 \tilde{G}_V + 4\pi R^2 \gamma$, where $\Delta \tilde{G}_V = \tilde{G}_{\text{chem}} + \tilde{G}_{\text{CS}}$. Here $\tilde{G}_V$ is the formation energy per molar volume of L₁₂-phase in fcc-Al, which is the sum of chemical formation energy $\tilde{G}_{\text{chem}}$ and the associated interfacial strain energy $\tilde{G}_{\text{CS}}$. The nucleation energy $\Delta G(R^*)$ and the critical radius R^* can be thus deduced to be $\Delta G(R^*) = \frac{16\pi}{3} \frac{\gamma^3}{(\Delta \tilde{G}_{\text{chem}} + \Delta \tilde{G}_{\text{CS}})^2}$ and $R^* = \frac{-2\gamma}{\Delta \tilde{G}_{\text{chem}} + \Delta \tilde{G}_{\text{CS}}}$.

Based on the precipitation reaction of $[\text{Al}_n\text{X}]_{\text{fcc}} \rightarrow \text{Al}_3\text{X}(\text{L}_{12}) + [\text{Al}_{n-3}]_{\text{fcc}}$, $\tilde{G}_{\text{chem}}$ can be approximated as

$$\begin{aligned} \Delta \tilde{G}_{\text{chem}} &= \tilde{G}(\text{Al}_3\text{X}) + (n-3)\mu_{\text{Al}}(\text{Al}) - \tilde{G}(\text{Al}_n\text{X}) \\ &= [\Delta \tilde{H}(\text{Al}_3\text{X}) - \Delta \tilde{H}(\text{Al}_n\text{X})] - T[\Delta \tilde{S}(\text{Al}_3\text{X}) - \Delta \tilde{S}(\text{Al}_n\text{X})], \end{aligned} \quad (3)$$

where $\Delta \tilde{H}(\text{Al}_3\text{X})$ and $\Delta \tilde{H}(\text{Al}_n\text{X})$ are the formation enthalpies per molar volume of L₁₂-Al₃X and fcc-Al_nX ($X = \text{Er/Zr}$) bulks, respectively. $\Delta \tilde{S}(\text{Al}_3\text{X})$ and $\Delta \tilde{S}(\text{Al}_n\text{X})$ are corresponding the formation entropies. $n = 107$ for the $3 \times 3 \times 3$ fcc-Al supercell model of dilute Al(X) solid solution. Recall that

configurational entropy is generally negligible for a dilute solid solution, and thermal electronic entropy is also negligible for relatively low temperatures, as clearly demonstrated for dilute Ni–Al [39] and Al–Sc alloys [40]. We thus considered only vibrational entropy in Eq. (3). The terms of $[\Delta \tilde{H}(\text{Al}_3\text{X}) - \Delta \tilde{H}(\text{Al}_n\text{X})]$ and $[\Delta \tilde{S}(\text{Al}_3\text{X}) - \Delta \tilde{S}(\text{Al}_n\text{X})]$ have been previously calculated as -0.867 eV and $3.528 k_B$ per Er atom for L₁₂-Al₃Er [41], and -0.776 eV and $2.67 k_B$ per Sc atom for L₁₂-Al₃Sc [22]. The coherent strain energies have been also calculated as 0.009 eV/atom for the Al/Al₃Er(L₁₂) [35] and 0.0038 eV/atom for the Al/Al₃Sc(L₁₂) [22], respectively. For a high aging temperature $T = 673$ K, the nucleation energy $\Delta G(R^*)$ and the critical nucleation radius R^* can be thus predicted as $\sim 5.4 \times 10^{-19}$ J and 8.4 Å for Al₃Er(L₁₂) [35] and $\sim 2.9 \times 10^{-19}$ J and 6.6 Å for Al₃Sc(L₁₂) [22] in Al, all consisting well with other calculations [42]. These results also suggest that, under the same aging conditions, L₁₂-Al₃Sc is more prone to precipitate than L₁₂-Al₃Er in Al, due to its lower $\Delta G(R^*)$ and smaller R^* .

3.3.2 Stabilities of L₁₂ nano-phases: core-shelled, homogeneous, vs. separately formed precipitates

It has been experimentally reported that the core-shelled ternary L₁₂-Al₃(Sc_xEr_{1-x}) nano-phases, rather than binary Al₃Sc(L₁₂) and Al₃Er(L₁₂), formed in dilute Al–Sc–Er alloys [14]. In the section, we extended the classic nucleation theory and first-principles calculations to evaluate various possible structures of ternary L₁₂-Al₃(Sc_xEr_{1-x}) nano-precipitates under a given aging temperature and Er/Sc atom ratio. Specifically, the possible ternary L₁₂-phase structures include the Al₃Er-core and Al₃Sc-shell structure (i.e., L₁₂-Al₃Sc(Er)), the Al₃Sc-core and Al₃Er-shell structure (i.e., the L₁₂-Al₃Er(Sc)), and the homogeneous random structure of L₁₂-Al₃(Sc_xEr_{1-x}). The ternary results were further compared with those of the separate nucleation of binary Al₃Sc(L₁₂) and Al₃Er(L₁₂) to ascertain the nucleation preference and the relative stabilities of L₁₂ nano-phases in dilute Al–Sc–Er alloys.

According to the classical nucleation theory, the total energy changes due to homogeneous nucleation of L₁₂ nano-phases can be calculated as

$$G_{\text{separate}} = \frac{4\pi}{3} (r^3 \Delta \tilde{G}_V^{\text{Al}_3\text{Er}} + r^3 \Delta \tilde{G}_V^{\text{Al}_3\text{Sc}}) + 4\pi (r^2 \gamma_{\text{Al}/\text{Al}_3\text{Er}} + r^2 \gamma_{\text{Al}/\text{Al}_3\text{Sc}}), \quad (4\text{-a})$$

$$G_{\text{Al}_3\text{Sc(Er)}} = \frac{4\pi}{3} ((R^3 - r^3) \Delta \tilde{G}_V^{\text{Al}_3\text{Sc}} + r^3 \Delta \tilde{G}_V^{\text{Al}_3\text{Er}}) + 4\pi (r^2 \gamma_{\text{Al}_3\text{Sc}/\text{Al}_3\text{Er}} + R^2 \gamma_{\text{Al}/\text{Al}_3\text{Sc}}), \quad (4\text{-b})$$

$$G_{\text{Al}_3\text{Er(Sc)}} = \frac{4\pi}{3} ((R^3 - r^3) \Delta \tilde{G}_V^{\text{Al}_3\text{Er}} + r^3 \Delta \tilde{G}_V^{\text{Al}_3\text{Sc}}) + 4\pi (r^2 \gamma_{\text{Al}_3\text{Sc}/\text{Al}_3\text{Er}} + R^2 \gamma_{\text{Al}/\text{Al}_3\text{Er}}), \quad (4\text{-c})$$

$$G_{\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})} = \frac{4\pi}{3}R^3\Delta\tilde{G}_V^{\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})} + 4\pi R^2\gamma_{\text{Al}/\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})}. \quad (4-d)$$

All energy terms in Eqs. (4) have been calculated in the previous sections, except $\Delta\tilde{G}_V^{\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})}$. It is still difficult to accurately calculate the volumetric formation enthalpy and vibrational entropy of a random-structured $\text{Al}_3(\text{Er}_x\text{Sc}_{1-x})$ from the first principles, we resorted to estimate $\Delta\tilde{G}_V^{\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})}$ as the composition-weighted summation of $\Delta\tilde{G}_V^{\text{Al}_3\text{Sc}}$ and $\Delta\tilde{G}_V^{\text{Al}_3\text{Er}}$. And similarly, due to the difficulty in constructing a $\text{Al}/\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})$ interface model, we estimated $\gamma_{\text{Al}/\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})}$ as the composition-weighted summation of $\gamma_{\text{Al}/\text{Al}_3\text{Sc}}$ and $\gamma_{\text{Al}/\text{Al}_3\text{Er}}$.

Figure 3 plots the calculated nucleation energies as a function of precipitate radius for various candidate structures under different aging temperatures and Er/Sc atom ratios. The most striking finding is that the core-shelled $\text{Al}_3\text{Sc}(\text{Er})$ structure has always the lowest nucleation energy among all possible precipitation structures, no matter the aging temperature and the Er/Sc ratio. This strongly indicates that the Al_3Er -core and Al_3Sc -shell structure is the most energy favored to form and thus shall dominate in popularity among all L_{12} nano-precipitates in $\text{Al}-\text{Sc}-\text{Er}$ alloys. It is also interesting that, for the ultrafine particle sizes ($R < \sim 1$ nm), all these structures have almost the same nucleation energy. Thus, it is very likely that various L_{12} nano-structures could coexist during the initial precipitation, especially under a lower Er/

Fig. 3 Calculated total nucleation energies versus the precipitate radius for four possible L_{12} -phase structures under various aging temperatures and Er/Sc ratios. The black curve is for the nucleation of two separated $\text{L}_{12}-\text{Al}_3\text{Sc}$ and Al_3Er particles, the blue curve for core-shelled $\text{L}_{12}-\text{Al}_3\text{Er}(\text{Sc})$ structure, the green curve for the homogeneous random $\text{L}_{12}-\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})$ structure, and the red curve for core-shelled structure of $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$

Sc ratio at a lower temperature as suggested in Fig. 3. That is to say, no dominant structure type shall be expected for ultrafine L_{12} nano-precipitates in $\text{Al}-\text{Sc}-\text{Er}$ alloys. We have no available experimental evidence on these regards, but such a thermodynamics-based prediction is in good accordance with an independent experimental finding for ternary $\text{Al}_3(\text{Er}_x\text{Zr}_{1-x})$ nano-precipitates in an $\text{Al}-\text{Mg}-\text{Er}$ alloy [43], i.e., the core-shelled structure becomes more prominent as the nano-precipitate size increasing. Other important insights can be also suggested from Fig. 3. (1) Similarly as we have previously predicted for $\text{Al}-\text{Sc}-\text{Zr}$ and $\text{Al}-\text{Er}-\text{Zr}$ alloys [22, 35], the formation of ternary L_{12} -phases is generally always more energy-preferred than binary L_{12} -phases in $\text{Al}-\text{Sc}-\text{Er}$ alloys, especially when increasing the aging temperatures or the Er/Sc ratio. (2) Increasing aging temperature and/or time helps approach the thermodynamic equilibrium, thereby to favor the dominant formation of the stable, core-shelled $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$ structure.

So far, we have gained profound insights for nucleation and relative stabilities of various possible L_{12} -phase nano-precipitates in dilute $\text{Al}-\text{Sc}-\text{Er}$ alloys. Thermodynamic driving force exists evidently in favor of the formation of the core-shelled $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$ structure, no matter the aging temperature and the Er/Sc ratio, especially for particle sizes $R > \sim 1$ nm. We also recall that solute Er or Sc in Al can dissolve into bulk phase $\text{L}_{12}-\text{Al}_3\text{X}$ ($\text{X} = \text{Sc}$ or Er), by favorably substituting at the X sublattice as we predicted in Table 1. Three basic mechanisms can be thus suggested from the first principles for the formation of the core-shelled $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$ structure. (1) The ternary nano-cluster precursor mechanism: random-structured ternary $\text{L}_{12}-\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})$ phases form directly from ternary atomic nano-clusters in Al matrix. (2) The binary-phase precursor mechanism: random-structured ternary $\text{L}_{12}-\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})$ phases form from primarily precipitated binary $\text{L}_{12}-\text{Al}_3\text{X}$ through the substitution of third element (Sc or Er) at the X sublattice. In both cases, the resulting random-structured ternary $\text{L}_{12}-\text{Al}_3(\text{Sc}_x\text{Er}_{1-x})$ phases are only meta-stable and can gradually evolve into the most thermodynamically stable core-shelled structure of $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$. (3) The interface segregation mechanism: the segregation of third element Sc to primarily precipitated $\text{Al}/\text{Al}_3\text{Er}(\text{L}_{12})$ interfaces results in a $\text{L}_{12}-\text{Al}_3\text{Sc}$ outer shell, and hence the most stable core-shelled structure of $\text{L}_{12}-\text{Al}_3\text{Sc}(\text{Er})$ as a direct consequence. In this sense, the $\text{Al}/\text{Al}_3\text{Er}(\text{L}_{12})$ interfaces role as heterogeneous nucleation sites for the $\text{L}_{12}-\text{Al}_3\text{Sc}$ outer shell. No direct experimental evidence is available to help distinguish between the latter two mechanisms that both require primarily precipitated binary L_{12} nano-phases as precursors. In the next section, we focused on the first-principles investigation of Sc segregation at $\text{Al}/\text{Al}_3\text{Er}(\text{L}_{12})$ interfaces. The calculated segregation energies of Sc were compared with

its substitution energies in L₁₂-Al₃Er nanoparticles, to assess the applicability of the latter two mechanisms.

3.4 Sc segregation at Al/Al₃Er(L₁₂) interfaces

We evaluated segregation energy as the total energy change due to one single solute Sc substitution at the Al or Er site of the Al/Al₃Er(L₁₂) interface as

$$\Delta G_{\text{seg}} = \left(G_{\text{Al/Al}_3\text{Er}}^{\text{Sc}} + \mu_i \right) - \left(G_{\text{Al/Al}_3\text{Er}} + \mu_{\text{Sc}} \right), \quad (4)$$

where $G_{\text{Al/Al}_3\text{Er}}$ and $G_{\text{Al/Al}_3\text{Er}}^{\text{Sc}}$ are the total energies of the interface supercells before and after Sc substitution, respectively. μ_i and μ_{Sc} are the chemical potentials of the substituted atom i (Al or Er) and the substituting atom Sc in the dilute Al solid solution. Coherent Al/Al₃Er(L₁₂) interfaces were considered with various different contacting facet relations, namely the (100)/(100), (110)/(110) and (111)/(111). Figure 4 shows the calculated segregation energies versus the relative position from the interface.

It is revealed in Fig. 4 that Sc substitution on the Al₃Er side of the Al/Al₃Er interface is energetically forbidden. The corresponding segregation energies are predicted as all positive and the values compare well with those of Sc

substitution for Er or Al in L₁₂-Al₃Er bulk (i.e., 0.038 or 1.954 eV/atom in Table 1, as the substituted Er or Al moves into the Al matrix). It is also obvious in Fig. 4 that matrix-dissolved Sc is prone to segregate to the Al/Al₃Er interface and substitute Al at dashed Er sites of layer No.1 on the Al side, no matter the contacting facets of the interface. This is certainly to favor the formation of a Sc-rich L₁₂-structured outer shell surrounding the Al₃Er inner core. The L₁₂-Al₃Sc outer shell with a sufficient thickness would effectively retard Er diffusion in and out, thus effectively reducing the coarsening kinetics of Al₃Er. Nevertheless, one notices that for the (100)/(100) interface, the Sc segregation energy of -0.5 eV/atom is still higher than the Sc substitution energy of -0.753 eV/atom in L₁₂-Al₃Er bulk (as the substituted Er stays within its L₁₂ bulk lattice in Table 1), while for the (110)/(110) or (111)/(111) interfaces, Sc segregation to the interface is much stronger, ~ -1 eV/atom. This implies that for the (100)/(100) interface, segregated Sc could more likely dissolve into the bulk interior of L₁₂-Al₃Er, and in this case, the L₁₂-Al₃Er core can hardly be Sc-free. This implication seems to be in good accordance with the 3D-APT measurement which evidently showed much enriched Sc at interface region along the [011] than along the [100] direction [14]. Neither the ternary nano-cluster precursor nor the binary-phase precursor mechanism can explain such an anisotropic distribution of elements. In either case, the nanoparticles shall have a more isotropically random structure. Only the interface segregation mechanism can explain well the atom profiles by 3D-APT. It thus becomes clear that the Er-rich core and Sc-rich shell structure of L₁₂-Al₃Sc(Er) is preferred by not only kinetics but also thermodynamics. Even with the same order of diffusivity, Er still diffuses four times faster than Sc in Al. The experimental finding that Er diffusivity decreased by three orders of magnitude when co-alloyed with Sc in Al shall be regarded as a direct consequence of the formation of the core-shelled L₁₂-Al₃Sc(Er) nanoparticles. A large amount of Er is entrapped inside the core region so that Er diffusion is greatly retarded in the matrix [14].

4 Conclusions

To clarify the thermodynamics governing the formation of core-shelled L₁₂ nano-precipitates in Al–Sc–Er alloys, we adopted first-principles DFT calculations to investigate all the energetics relevant to bulk substitution, interface formation, interface strain and segregation. The precipitation and relative stabilities of various L₁₂-phase nano-structures were then evaluated based on classic nucleation theory, for various different Er/Sc ratios and aging temperatures. From the above results, the following conclusive remarks can be made.

Fig. 4 **a** Al(001)/Al₃Er(001) interface structure and possible segregation sites for Sc. Blue balls denote Al atoms, and orange balls and dashed orange circles denote Er atoms or Er sites for segregated Sc, respectively. **b** Calculated segregation energies for Sc at different atomic layers near the Al(001)/Al₃Er(001), Al(110)/Al₃Er(110) or Al(111)/Al₃Er(111) interface

- (1) Only matrix-dissolved Sc (or Er) can substitute the X sublattice sites in $L1_2$ - Al_3X ($X=Er$ or Sc). The inter-substitution between $L1_2$ - Al_3Er and Al_3Sc is energetically forbidden. The lattice misfits are small ($\sim 3.0\%$ only), and the interface energies of $Al_3Er(L1_2)/Al_3Sc(L1_2)$ are nearly zero for various contacting facets. All these results strongly suggest the $Al_3Er(L1_2)/Al_3Sc(L1_2)$ interface can easily form as a sharp, highly coherent interface.
- (2) $Al_3Sc(L1_2)$ shall precipitate in preference to $Al_3Er(L1_2)$ from the Al matrix. The critical radius and work of nucleation are predicted as $6.6 \text{ \AA}$ and $\sim 2.9 \times 10^{-19} \text{ J}$ for $Al_3Sc(L1_2)$, which is much lower than that those of $Al_3Er(L1_2)$ ($8.4 \text{ \AA}$ and $\sim 5.4 \times 10^{-19} \text{ J}$).
- (3) No matter aging temperature and the Er/Sc ratio, core-shelled $L1_2$ - $Al_3Sc(Er)$ is always predicted as the most stable structure and shall account for the majority of nano-precipitates with a radius of $> 1 \text{ nm}$. For those nano-precipitates of $< 1 \text{ nm}$, various different structures may coexist and no any specific structure type could be predominant in number.
- (4) Matrix-dissolved Sc can strongly segregate to the Al/ Al_3Er interface, especially for (110) and (111) interface. A Sc-rich shell can be resulted and role as a barrier for Er diffusion in and out. The interface segregation mechanism shall be thus responsible for the formation of core-shelled $Al_3Sc(Er)$ structure which is preferred by not only kinetics but also thermodynamics in dilute Al-Sc-Er alloys.

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