The Phase Stability of Al$_3$Er Studied by the First-Principles Calculations and Experimental Analysis

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Abstract: The thermodynamics of five Al$_3$Er compounds were investigated through first-principles density-functional theory (DFT) and experimental analysis. The Al$_3$Er compounds with Al$_3$Ho.hR20 (prototype Al$_3$Ho, Pearson symbol hR20), Cu$_3$Au.cP4, AlNd$_3$hP8, Ni$_3$Ti.hP16 and Al$_3$Gd.hR12 structures exhibited formation energies of −0.412(−0.417), −0.411(−0.416), −0.400(−0.413), −0.399(−0.345) and −0.342(−0.345) meV/atom when using DFT with “standard” potential (“frozen core” potential) of Er. The results indicated that the Al$_3$Ho.hR20 structure was the thermodynamic stable phase and the other structures were metastable. The formation energy of Cu$_3$Au.cP4 structure was only 1 meV/atom less than that of Al$_3$Ho.hR20. Experimentally, the Al-30 wt.% Er alloys were cooled from 900 °C to 500 °C at the rate of 5 ± 2 °C/h and 60 ± 2 °C/h, respectively. The corresponding XRD analysis showed that the Al$_3$Ho.hR20 was formed at the cooling rate of 5 ± 2 °C/h and the Cu$_3$Au.cP4 was formed at the cooling rate of 60 ± 2 °C/h, which indicated that the Al$_3$Ho.hR20 was in a thermodynamic stable phase and the Cu$_3$Au.cP4 was in a metastable phase with high stability. The structural analysis indicated that the tiny energy difference between Al$_3$Ho.hR20 and Cu$_3$Au.cP4 might be attributed to a similar structure with varied stacking sequences.

Keywords: Al$_3$Er; phase stability; first-principles

1. Introduction

Micro-alloying is one of the efficient approaches utilized to improve strength and to increase the recrystallization temperature of aluminum alloys. By adding several transition or rare-earth elements, nanoscale coherent stable Cu$_3$Au.cP4 structure Al$_3$M particles can precipitate in aluminum alloys from supersaturated aluminum solid-solution, resulting in an increase in strength and the recrystallization temperature [1–3]. Sc is the most widely studied micro-alloying element, because the Cu$_3$Au.cP4 structure Al$_3$Sc precipitated from supersaturated Al-Sc alloys could lead to a considerable increase of the strengthening in Al alloys [1]. However, the high cost of Sc inhibited the industrial application of Al-Sc alloys. Er was considered to be one of the potential substitutional elements, since Al$_3$Er with the same Cu$_3$Au.cP4 structure could precipitate during the heat treatment of Al-Er alloys [4–6].

The Al$_3$Er precipitates with Cu$_3$Au.cP4 structure was considered as the thermodynamic stable phase in the Al-Er binary phase diagram [7,8] or ternary system [9,10]. However, it was reported earlier [11] that, when the Al-20 wt.% Er alloy was cooled from 900 °C to 500 °C at the rate of 85 °C/h and 4 °C/h, the Al$_3$Er phase was found in Cu$_3$Au.cP4 and Al$_3$Ho.hR20 structure, respectively.

Theoretically, the stabilities of varied structures of Al$_3$Er were evaluated with different methods. A criteria was supposed by Vucht [12] that the thermodynamic stable Al$_3$M
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(M = Lanthanide series rare earth) phases was determined by the radius ratio of Al/M. The stable phase of Al₃Er was determined to be of Cu₃Au.cP4 structure, and Al₃Er was actually located between Al₃Ho.hR20 and Cu₃Au.cP4 structure. Gao et al. [13] calculated the formation energies of Al₃Er phase in Al₃Ho.hR20, Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures at 0 K using first-principles with “frozen core” pseudopotentials. The pseudopotentials kept 11 4f electrons frozen in the core (“frozen core” potentials. FC) and Er was treated as 3-valence. The results showed that Al₃Er in hR20 structure was thermodynamically stable and Al₃Er in Cu₃Au.cP4, AlNd₃.hP8, Al₃Gd.hR12 and Ni₃Ti.hP16 structures were metastable. Mao et al. [14] calculated formation energies of Al₃Er in Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures, using the “frozen” potentials and taking the magnetic part into account. The results showed that Cu₃Au.cP4 structure was the most stable phase among those four structures. The two theoretical calculation results were not consistent with each other completely, due to whether the influence of 4f electrons is considered. For the “frozen core” potential of Er, 4f electron is not considered in the calculation, which can save on computational demand very well. However, for the “standard” potential of Er, 4f electron is considered, which may grant more accurate results.

In this paper, phase stability of the ground state of the intermetallic compound Al₃Er was investigated by both the first-principles calculation based on density functional theory and experimental method. The formation energies of Al₃Er compounds with Al₃Ho.hR20, Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures were evaluated, respectively, with “standard” potential and “frozen core” potential for Er. To access the zero-point energy of phonon contribution to the phase stability. We compute the phonon properties of Cu₃Au.cP4 and Al₃Ho.hR20 Al₃Er. To obtain the thermodynamically stable phase in experiment, hypereutectic composition Al-30 wt.% Er alloy was melted and solidified from 900 °C to 500 °C with cooling rates of 60 ± 2 °C/h and 5 ± 2 °C/h, respectively. The corresponding XRD was performed to identify the structure of the formed Al₃Er phase.

2. Computation and Experiment Method

2.1. Computation Theory

For the thermodynamic properties of a given defect-free nonmagnetic material system at temperature T (in Kelvin) and volume V, within DFT, we can decompose the Helmholtz free energy as follows [15]:

\[ F(V, T) = E_{\text{eq}}(V) + F_{\text{el}}(V, T) + F_{\text{ph}}(V, T) + F_{\text{el-ph}}(V, T) + F_{\text{el-\text{ph}}}(V, T) \tag{1} \]

In the ab initio frame, \( E_{\text{eq}}(V) \) was the ground state energy at 0 K, \( F_{\text{el}}(V, T) \) came from electronic free energy, \( F_{\text{ph}}(V, T) \), \( F_{\text{el-ph}}(V, T) \) and \( F_{\text{el-\text{ph}}}(V, T) \) were the quasiharmonic, anharmonic and electron-phonon coupling free energy [15,16]. For solid systems, the contribution from electronic, pressure, volume, anharmonic approximation was a smaller magnitude of order than that of the ground state energy [15], which would be neglected in computing formation energies. In the harmonic approximation, zero-point energy (ZPE) may affect the stability calculations, cannot be neglected. Based on the above analysis, the relative phase stability properties of a binary compound was in comparison with the formation enthalpy difference which contained ground state energy and ZPE between compounds with different structure and the same composition [17–22]. The compound and its constituents in their equilibrium crystal structures were at 0 K. Therefore, the formation enthalpy (eV/atom) of Al₃Er compounds could be calculated as:

\[ \Delta H_{\text{ord}}^{\text{eq}}(\text{Al}_3\text{Er}) = E_{\text{Al}_3\text{Er}} - \left[ \frac{3}{4} E_{\text{eq}}(\text{Al}) - \frac{1}{4} E_{\text{eq}}(\text{Er}) \right] \tag{2} \]

where the \( H_{\text{ord}}^{\text{eq}}(\text{Al}_3\text{Er}) \), \( E_{\text{eq}}(\text{Al}) \) and \( E_{\text{eq}}(\text{Er}) \) are the sum of ground state energies and ZPE (per atom) of the compound \text{Al}_3\text{Er} and constituents, after Al and Er were relaxed to their
equilibrium and zero-pressure geometries, respectively, and 3/4, 1/4 were the composition of Al and Er in the compound.

2.2. Computational Details

The first-principles calculations were based on DFT and with projector-augmented plane-wave (PAW) method [23] as implemented in Vienna ab initio simulation package (VASP, version 5.3) [24,25]. The exchange-correlation energy function used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [26,27]. In the calculations, all structures were fully relaxed with respect to the cell lattice vector and inner atomic coordinates by minimizing the total energy until less than 1 meV. The convergence of energy with respect to the energy cutoff and k-mesh point were tested carefully. A plane-wave basis set was set as 360 eV, a 0.13 Å\(^{-1}\) spacing Monkhorst-Pack [28,29] k-mesh was used in the integration over the Brillouin zone for all calculations. Unless otherwise specified, for relaxations, the reciprocal space energy integration was performed by 1-ordered Methfessel–Paxton [30] technique with sigma of 0.05 eV. For the final static calculations of total energies, the tetrahedron method was used, corrected by Blöchl [31]. In the relax calculations, all the atomic configuration was assumed to be converged when the Hellman–Feynman forces were smaller than 0.0001 eV/Å. In the relax calculation and static calculations, the total energy was converged within 10\(^{-6}\) eV.

Er and its trialuminide displayed ferromagnetism or antiferromagnetic at lower temperatures and paramagnetism at temperature above 300 K [32,33]. Therefore, it could be treated as paramagnetism in calculations. In the present VASP’s pseudopotentials dictionary, there were three types of potentials for the Er element. The first one included the partial 4f electrons within the core level and its valence was 2, valence state 5p\(^{6}\)6s\(^{2}\) for Er. The second pseudopotential for Er with 4f-electrons in the core level and its valence was 3+ (so-called “frozen core” potential), whose valence state was 5p\(^{6}\)5d\(^{1}\)6s\(^{2}\). The third potential treated Er as 3+, whose valence state was 4f\(^{11}\)5s\(^{2}\)5p\(^{6}\)5d\(^{1}\)6s\(^{2}\) (so-called “standard” potential. ST) treated all the 4f electrons in the valence band.

Because some experiments and theory confirmed the 4f and 5d electrons could be hybridized for Er, partial 4f electrons could form bonds with other elements [34–38]. Usually, Er was treated as 3+ in calculations, instead of 2+ [13,38]. Therefore, treating Er as valence of 2 could not assess the 4f effect on structure’s calculation and thermal properties accurately. For the FC potential, treating Er as 3+ could save computational demanding very well, in approximation to the out-valence electron distribution, which was applied in many calculations [13,14,39,40]. The electron distribution of ST potential close to the real 4f-electron distribution in the Er element could assess the 4f-electron effect on thermodynamic property calculations, accurately. In this study, in order to illustrate whether the f-electrons affected thermodynamic phase stability of Al\(_3\)Er phase, both the “standard” and “frozen core” potential were used.

In this work, the phonon contribution at zero point was also predicted by using the Phononpy [41] simulation package based on the second (harmonic) force constants. The harmonic force constant is calculated using the direct approach base on the finite displacement method. We tested the convergence of the harmonic force constant with a 3 × 3 × 3 supercell of Al, Er and Cu\(_3\)Au.cP4 Al\(_3\)Er primitive cell, 2 × 2 × 2 supercell of Al\(_3\)Ho.hR20 Al\(_3\)Er primitive cell, to ensure the convergency of the results. In the ZPE calculation, we found a relative shift (0.25, 0.25, 0.25) with respect to the Γ point, and an interpolation mesh of 30 × 30 × 30 grids points of Al, Cu\(_3\)Au.cP4 Al\(_3\)Er, 36 × 36 × 27 grids points of Er, 35 × 35 × 30 grids points of Al\(_3\)Ho.hR20 Al\(_3\)Er, the ZPE was valid down to 0.05 meV/atom. Because the self-consistent calculation of supercell—while using the ST potential—could not be achieved, we used the FC potential for Er elements. Furthermore, configurational effects, which may arise from defects in the structure, could stabilize the structures when the temperature is not zero. Experimentally, Cu\(_3\)Au.cP4 structure Al\(_3\)Er was a common precipitate in aluminum alloy, but its microstructure has not been observed as bulk material. For Al\(_3\)Ho.hR20 structure Al\(_3\)Er, its microstructure has not been studied
so far. In this study, we didn’t consider configurational effects in the calculation process for simplification. Thereafter we would carry out the solidification experiments on Al-30 wt.% Er alloy with different cooling rates to ascertain the thermodynamically stable phase. For the details, see below.

2.3. Experimental Method

The alloys with nominal composition of Al-30 wt.% Er were brought from Hunan Rare Earth Metal Materials Research Institute. Its composition was measured to be Al-29.45 wt.% Er by X-ray fluorescence measurement. They were firstly cut into blocks and put into an alumina crucible with a diameter of 25 mm. Then they were sealed in quartz tube protected by argon gas with a vacuum of $10^{-3}$ Pa. The specimens were heated to 1000 °C and kept for 60 min, then cooled to 900 °C above the liquidus [7,8], and then to 500 °C below the eutectic temperature [7,8] at the cooling rate of 60 ± 2 and 5 ± 2 °C/h, respectively. The cooling rate curves are indicated in Figure 1.

Figure 1. Scheme of heat treatment of Al-30 wt.% Er, cooling rate of 60 ± 2 °C/h and 5 ± 2 °C/h, respectively.

The structures of the samples with two different cooling rates were analyzed using X-ray diffractometry (XRD D8 advance, Bruker, Karlsruhe, Germany) with Cu Kα radiation with wavelength of 1.5406 Å, current of 30 mA and voltage of 35 kV. The scanning speed was 4 degrees/min.

3. Results

3.1. Computational Results

Since the Al$_3$Er precipitates were observed in the structure of Cu$_3$Au.cP4 and Al$_3$Ho.hR20 structures experimentally [12,42,43], and the corresponding lattice parameters were measured, we firstly verified two kinds of potential of Er by comparing the experimental value of lattice parameters with calculated ones by relaxation of Al$_3$Er with these two structures. The relaxed lattice constants using treating the 4f-electrons in the core band (“frozen core” potential) or valence band (“standard” potential, ST) were listed in Table 1. For Cu$_3$Au.cP4 structure, the calculated lattice constants were 4.238 Å and 4.215 Å by using “frozen core” and “standard” potential, respectively. As listed in Table 1, the lattice parameter of Al$_3$Er with Cu$_3$Au.cP4 structure was 4.215 Å [12], 4.212 ± 0.002 Å [42] and 4.214 Å [43] from several reports. Table 1 also presents detailed comparisons between calculations and experimental results of lattice constants. We found that the difference between the calculation results of lattice constants at 0 K and the experimental result at ambient temperature is within 1%, which indicates that the lattice constants calculated by both frozen core potential of Er and standard potential of Er were acceptable.
Table 1. The calculated and experimental lattice constants of $\text{Al}_3\text{Er}$ in $\text{Cu}_3\text{Au.cP4}$ and $\text{Al}_3\text{Ho.hR20}$ structures with different potentials.

| Structure         | Lattice Constants/ Å | Difference/% |
|-------------------|----------------------|--------------|
|                   | ST       | FC       | EXP       | ST       | FC       |
| $\text{Cu}_3\text{Au.cP4}$ | 4.215   | 4.238    | 4.212 ± 0.002 [42] | 0.0     | 0.5     |
| $\text{Al}_3\text{Ho.hR20}$ | 5.993   | 6.063    | 6.025 [12]     | −0.5    | 0.6     |

Based on the verification of the Er potential, relaxation of the $\text{AlNd}_3.hP8$, $\text{Ni}_3\text{Ti.hP16}$ and $\text{Al}_3\text{Gd.hR12}$ structures were performed by using “standard” potential and “frozen core” potential. After relaxation calculation on each structure, static calculations were performed to get the formation energy. The main results of formation energy and relative energy by using different potentials of this paper were summarized in Table 2.

Table 2. The formation energy and other properties of $\text{Al}_3\text{Er}$ in different structures with different potentials.

| Structure         | Formation Energy with ST | Formation Energy with FC | Relative Energy |
|-------------------|--------------------------|--------------------------|----------------|
|                   | eV/atom                  | eV/atom                  | ST     | FC     |
| $\text{Al}_3\text{Ho.hR20}$ | −0.412                  | −0.417 **                 | 0      | 0 **   |
| $\text{Cu}_3\text{Au.cP4}$ | −0.411                  | −0.416 *                 | 0.001  | 0.001 * |
| $\text{Al}_3\text{Gd.hR12}$ | −0.400                  | −0.413 *                 | 0.012  | 0.004 * |
| $\text{AlNd}_3.hP8$     | −0.399                  | −0.345 *                 | 0.013  | 0.072 * |
| $\text{Ni}_3\text{Ti.hP16}$ | −0.342                  | −0.345 *                 | 0.060  | 0.072 * |

* without ZPE correction. ** with ZPE correction.

From Table 2, it was clearly seen that the formation energy of $\text{Al}_3\text{Er}$ with $\text{Al}_3\text{Ho.hR20}$ structure of $-0.412$ eV/atom and/or $-0.417$ eV/atom was the lowest formation energy, indicating that the $\text{Al}_3\text{Ho.hR20}$ structure was the thermodynamic stable phase. Also, the formation energies of $\text{Al}_3\text{Ho.hR20}$ structure by using different potential were set to zero. Then the relative energies of other four structures compared with the formation energy of $\text{Al}_3\text{Ho.hR20}$ were listed in the fourth and fifth columns of Table 2. It could be found that the formation energy differences of $\text{Cu}_3\text{Au.cP4}$, $\text{Al}_3\text{Gd.hR12}$ and $\text{AlNd}_3.hP8$ were less than the room temperature thermal energy ($k_B T = 26$ meV/atom) [13], suggesting that all of them were thermodynamically metastable. Especially among all the metastable phases, $\text{Cu}_3\text{Au.cP4}$ structure was of the lowest formation energy, only 1 meV/atom above the $\text{Al}_3\text{Ho.hR20}$, indicating the most energetically favorable metastable phase. This result was in agreement with the results proposed by Gao et al. [13]. In Table 2, we also show the calculation results of $\text{Al}_3\text{Ho.hR20}$ and $\text{Cu}_3\text{Au.cP4} \text{Al}_3\text{Er}$ when ZPE correction was considered. The difference of formation energy between the $\text{Al}_3\text{Ho.hR20}$ and $\text{Cu}_3\text{Au.cP4} \text{Al}_3\text{Er}$ changed from 0.001 eV/atom to 0.008 eV/atom, which became larger. Although the difference is still small, the results did show that $\text{Al}_3\text{Ho.hR20}$ was the thermodynamically stable structure of $\text{Al}_3\text{Er}$. The relative formation energies of $\text{Al}_3\text{Gd.hR12}$ were 12 and 4 meV/atom with “standard” potential and “frozen core” potential, lower than one half of the room temperature thermal energy, which implied that the $\text{Al}_3\text{Gd.hR12}$ was in an energetically favorable metastable phase. For the $\text{AlNd}_3.hP8$ and $\text{Ni}_3\text{Ti.hP16}$ structure, by “frozen core” potential, both structures have the same formation energy of
72 meV/atom. However, by the “standard” potential, the formation energy of AlNd₃.hP8 was 13 meV/atom, the formation energy of Ni₃Ti.hP16 was 60 meV/atom. Thus, it was shown that the “standard” potential did not lead to a different sequence of the relative stability but did affect the values of relative formation energies.

3.2. Experimental Results

Hypereutectic alloy was selected with the composition of Al-30 wt.% Er, and the Al₃Er phase was formed from the liquid directly. After solidification with the cooling rate of 60 ± 2 °C and 5 ± 2 °C/h from 900 °C to 500 °C, the alloy was analyzed by XRD and the results were shown in Figure 2. Figure 2a was the XRD spectrum of the sample formed with a cooling rate of 60 ± 2 °C/h. It could be found that the peaks were from the Cu₃Au.cP4 type Al₃Er and FCC Al. Figure 2b shows the XRD spectrum of the sample formed with a cooling rate of 5 ± 2 °C/h. The peaks were from the Al₃Ho.hR20 structure Al₃Er and FCC Al.

![Figure 2. XRD spectrum of Al-30 wt.% Er for cooling rate of (a) 60 ± 2 °C/h and (b) 5 ± 2 °C/h, respectively.](image)

The results indicated that the Cu₃Au.cP4 structure Al₃Er formed in the alloy with a higher cooling rate of 60 ± 2 °C/h, while the Al₃Ho.hR20-structured Al₃Er formed with a lower cooling rate of 5 ± 2 °C/h. The only difference between these two processes was the cooling rate, and the latter was closer to an equilibrium state. Hence, the Al₃Ho.hR20 was the thermodynamically stable structure, and Cu₃Au.cP4 was the very stable metastable structure.

4. Discussion

From the above formation energy calculation results, Al₃Er with five crystal structures were of close negative values, indicating large thermodynamic trends for formation of all the five structures. Among them, Al₃Ho.hR20 structure was of the most negative formation energy, and Cu₃Au.cP4 was of only 1 meV less value. The thermodynamic stable phase with Al₃Ho.hR20 structure was confirmed by solidification of Al-30 wt.% Er alloy with the very low cooling rate of 5 ± 2 °C/h, and the metastable phase with Cu₃Au.cP4 structure was easily formed with higher cooling rate of 60 ± 2 °C/h.
The very small difference in formation energy between Al₃Ho.hR20 and Cu₃Au.cP4 structure could be discussed from the point view of the crystal structure. Both structures could be constructed by stacking the close-packed planes but with different sequences, as shown in Figure 3. In Figure 3a, we show the side view of [110] plane with an atom in the plane passing through the (0,0,0) (large size) and (0.5,0.5,0) point (small size), normal to the [111] plane of Cu₃Au.cP4 Al₃Er. In Figure 3b, we show the [100] plane with atom in the plane passing through the (0,0,0) (large size) and (0.5,0,0.5) point (small size), normal to the [112] plane of Al₃Ho.hR20 Al₃Er. From Figure 3, it can be seen that the stacking sequence of Cu₃Au.cP4 was 3-layer ABC, while that of the Al₃Ho.hR20 structure was a 15-layer ABCBCBCACACABAB. The similar structure with only varied stacking sequence could lead to a tiny formation energy difference between these two structures.

![Side view of the stacking sequences for Al₃Er with (a) Cu₃Au.cP4 and (b) Al₃Ho.hR20 structure.](image)

**Figure 3.** Side view of the stacking sequences for Al₃Er with (a) Cu₃Au.cP4 and (b) Al₃Ho.hR20 structure.

5. Conclusions

The formation energies of Al₃Ho.hR20, Cu₃Au.cP4, AlNd₃.hP8, Ni₃Ti.hP16 and Al₃Gd.hR12 structures at 0 K were calculated based on first principles using “Standard” potential and “frozen core” potential for Er. When taking the vibrational effect into account, the difference of formation energy between the Al₃Ho.hR20 and Cu₃Au.cP4 structure Al₃Er was changed from tiny 0.001 eV/atom to 0.008 eV/atom, indicating that Al₃Er with Al₃Ho.hR20 structure was thermodynamically stable phase, while that with Cu₃Au.cP4 structure was the most stable metastable phase.

Experimentally, the solidification of Al-30 wt.% Er alloy showed that the Cu₃Au.cP4 structure Al₃Er formed in the alloy with a cooling rate of 60 ± 2 °C/h, while the Al₃Ho.hR20-structured Al₃Er formed with very low cooling rate of 5 ± 2 °C/h, which proved that the thermodynamic stable phase was a Al₃Ho.hR20 structure, in good agreement with the theoretical calculation result.

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