



# Article First-Principles Investigation of the Diffusion of TM and the Nucleation and Growth of L1<sub>2</sub> Al<sub>3</sub>TM Particles in Al Alloys

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Abstract: The key parameters of growth and nucleation of Al<sub>3</sub>TM particles (TM = Sc-Zn, Y-Cd and Hf-Hg) have been calculated using the combination of the first principles calculations with the quasi-harmonic approximation (QHA). Herein, the diffusion rate  $D_s$  of TM elements in Al is calculated using the diffusion activation energy Q, and the results show that the  $D_s$  of all impurity atoms increases logarithmically with the increase in temperature. With the increase in atomic number of TM, the D<sub>s</sub> of 3–5d TM elements decreases linearly from Sc, Y and Hf to Mn, Ru and Ir, and then increases to Zn, Ag and Au, respectively. The interface energy  $\gamma_{\alpha/\beta}$ , strain energy  $\Delta E_{cs}$ , chemical formation energy variation  $\Delta G_V$  and surface energy  $E_{sur}^{ave}$  were further computed from the based interface and slab models, respectively. It was found that, with the increase in the atomic number of TM, the interface energies  $\gamma_{\alpha/\beta}$  of Al/Al<sub>3</sub>TM (TM = (Sc-Zn, Y-Cd)) decreased from Sc and Y to Mn and Tc and then increased to Zn and Cd, respectively (except for the (001) plane of Al/Al<sub>3</sub>(Fe-Co), the (111) plane of Al/Al<sub>3</sub>Pd and the (110) and (111) planes of Al/Al<sub>3</sub>Cd). The strain energies  $\Delta E_{cs}$  of Al/Al<sub>3</sub>TM (TM = (Sc-Zn)) increased at first, and then decreased for all cycles. The chemical formation energy  $\Delta G_V$  of all Al<sub>3</sub>TM changed slightly in the temperature range of 0~1000 K, except that the  $\Delta G_V$  of Al<sub>3</sub>Sc, Al<sub>3</sub>Cu, Al<sub>3</sub>(Y-Zr), Al<sub>3</sub>Cd, Al<sub>3</sub>Hf and Al<sub>3</sub>Hg increased nonlinearly. With the increase in atomic number at both 300 and 600 K, the  $\Delta G_V$  of 3–5d TM elements increased from Sc, Y and Hf to Mn, Tc and Re at first, and then decreased to Co, Rh and Ir, respectively, and slightly changes at the end. With the increase in atomic number of TM, the variation trends of the surface energies of Al<sub>3</sub>TM intermetallic compounds present similar changes for all cycles, and the (111) surface always has the lowest values.

Keywords: DFT framework; nucleation and growth; diffusion behavior; L12 Al3TM

# 1. Introduction

Al-based alloys have been widely applied in the electronics, aerospace and automotive industries due to their low density, high specific strength and welding strength [1]. Adding transition elements (TMs) can significantly improve the mechanical and thermodynamic properties of Al alloys [2–6]. For example, the existence of Sc (0.3%) in the Al matrix increases the ultimate rupture strength of annealed Al sheets from 55 to 240 MPa [7], and L1<sub>2</sub>-Al<sub>3</sub>Zr in the Al matrix is used as a grain refiner to improve the coarsening resistance and creep properties [8,9]. However, the high cost of Sc and Zr limits their applications in commercial Al alloys. Specifically, intermetallic compounds with TMs are suitable candidates for high temperature applications, as the crystal types in the Al matrix may be L1<sub>2</sub>, D0<sub>22</sub>, D0<sub>23</sub> or D0<sub>19</sub> structures [8,10–12], of which the L1<sub>2</sub> phase is an important



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). intermetallic compound and has been widely studied [13–16]. Moreover, the TMs can be used to substitute the expensive Sc and Zr elements in  $L1_2$ -Al<sub>3</sub>Sc and Al<sub>3</sub>Zr.

The previous research proved that fixing the dislocations and grain boundaries can effectively refine the deformed and recrystallized grains, depending on the dispersed distribution of L1<sub>2</sub> Al<sub>3</sub>TM particles during rising heat [17,18]. The diffusion rate of TM solute atoms in an Al matrix and the interfacial properties of Al<sub>3</sub>TM/Al are important parameters for the investigation of nucleation, the growth of L1<sub>2</sub> Al<sub>3</sub>TM phases [19–21], and the low-index bonds of particles to matrix [22,23]. However, the experimental exploration of appropriative substitution TMs is difficult because of the complex environment and the expensive cost [15,23–28]. Fortunately, in recent years, with the development of modern computer technologies, theoretical identification (e.g., first-principles (FP) calculations based on density functional theory (DFT) [15]) in the complicated systems (e.g., metals and ceramics) has become the most powerful method to accomplish this [29–32].

The stability and nucleation behavior of L1<sub>2</sub>-Al<sub>3</sub>Sc and Al<sub>3</sub>Li binary phases have first been investigated using the framework of density functional theory (DFT) calculation by Mao et al. [15]. Their results showed that the L1<sub>2</sub>-Al<sub>3</sub>Sc and Al<sub>3</sub>Li structures have lower formation energies than those of the corresponding  $D0_{23}$ ,  $D0_{19}$  and  $D0_{22}$  structures. Furthermore, they found that the interface and strain energies of Al<sub>3</sub>Sc are much higher than those of Al<sub>3</sub>Li for all (001), (110) and (111) interfaces. Zhang et al. [33] have comprehensively studied the solubility of RE (RE = Y, Dy, Ho, Er, Tm and Lu) in Al based on the free energy difference between L1<sub>2</sub> bulk and Al solid solution matrix in the DFT theoretical framework. Their results indicated that the solubility of all rare earth (RE) (RE = Y, Dy, Ho, Er, Tm and Lu) elements increases with the increase in temperature (~1000 K). They also believed that Dy and Y elements can become better candidates for Sc due to the better stability of Al<sub>3</sub>Dy and Al<sub>3</sub>Y compounds and their almost identical solubility compared to the higher-cost Sc element. Sun et al. [34] have calculated low-index (001), (110) and (111) surface energies of  $L_{12}$ -Al<sub>3</sub>Sc particles adopting slab model with 15 A vacuum region. Their results show that when the surface energies of non-stoichiometric (001) and (110) surfaces of  $Al_3Sc$ are calculated, their values should be considered as different under different Al chemical potentials, and in a wide range of Al chemical potentials, the surface energies of the (111) surface with AlSc-terminated have lower values, indicating that they are more stable than other surfaces.

However, up to date, the diffusion rates  $D_s$  of TMs in Al, the surface properties of L1<sub>2</sub>-Al<sub>3</sub>TM and the interface of Al<sub>3</sub>TM/Al-matrix have not been systematically investigated. Specifically, the nucleation and growth of L1<sub>2</sub>-Al<sub>3</sub>TM (TM = Sc-Zn, Y-Ag, Hf-Au) particles at finite temperatures have not been obtained, and their relationship to the atomic number of TM hasn't been described in detail due to the large computational cost required. In the present work, by combining the first-principles calculations with the quasi-harmonic approximation (QHA), the relationship between the particles' nucleation/growth and atomic number/temperature are discussed. First, the diffusion rates  $D_s$  of TMs as a functional of atomic number and temperature have been researched. Then, the relationship between the driving force and the hindrance of particle nucleation and the atomic number of TM is explained based on the interface model. Finally, the effects of the surface stability of different intermetallic compounds with the change in atomic number based on the slab model are obtained.

## 2. Computed Methods

All calculations in this work were performed in Vienna ab initio Simulation Package (VASP) [34] with the 5.4.4 version, which adopts the framework of density functional theory (DFT) [35] calculations to solve the Kohn–Sham equation and obtain the total energy from different models. In the calculated processing of VASP, to relax all models to their most stable ground state, the electron–core interaction was described by the projector augmented wave (PAW) [36] method. The optimal choice of exchange–correlation functional was considered using the generalized gradient approximation (GGA) with the Perdew–Burke–

Ernzerh (PBE) version [31]. A 10 × 10 × 10 k-point sampling grid with the Gammacentered Monkhorst–Pack method [37] in the first Brillouin zone was selected via strict convergence testing (see Figure 1) for bulk properties calculation. A cut off energy of the plane-wave basis of 500 eV was chosen for the whole calculated process. The energy and force tolerance were set to  $10^{-7}$  eV and 0.01 eV/Å, respectively, by using conjugate gradient (CG) minimization and Broyden–Fletcher–Goldfarb–Shannon (BFGS) schemes [38].



Figure 1. The total energy of Al<sub>3</sub>Sc as a function of k-point sampling grids.

Here, based on the slab model, we investigated three low-index surfaces, containing (100), (110) and (111) surfaces of Al and L1<sub>2</sub>-Al<sub>3</sub>TM, which adopted 14, 14 and 16 layers, respectively [24,39]. All interfaces of (100), (110) and (111) surfaces of Al/L1<sub>2</sub>-Al<sub>3</sub>TM are calculated by using the 18 layers interface model. A  $10 \times 10 \times 1$  k-mesh grid for both cases was tested to be suitable for this work. To simulate diffusion behavior, we constructed a  $3 \times 3 \times 3$  supercell with  $4 \times 4 \times 4$  k-mesh grids to obtain the diffusion barriers of the solute diffusion of TMs in the Al matrix based on the climbing-image nudged elastic band (CI-NEB) [40] method. Meanwhile, a spring force constant of 5 eV/Å was considered to keep all the images separated, and these CI-NEB iterations were continued until the forces on each atom were less than 0.05 eV/Å.

#### 3. Conclusion Description

# 3.1. Diffusion

In the process of heating up, some atoms will detach from their original equilibrium positions and then diffuse to a new site while obtaining enough energy. Thus, the diffusion behavior is a common phenomenon in the field of material science and engineering. According to the Lifshitz and Slyozov and Wagner methods [41,42], the growth of particles is affected by the diffusion behavior of solute atoms, and the faster diffusion in the Al matrix is beneficial for the grain growth. In the current work, to investigate diffusion behavior, we first show a vacancy-substitution model, as depicted and visualized in Figure 2a by VESTA codes. The vacancy-substitution model can be divided into two types: the self-diffusion of the violet Al atom and the impurity diffusion of the TM pink ball [24,39]. The black arrow represents the diffusion path for the TM atom. To further investigate the diffusion behavior, the diffusion coefficient as a function of jump frequency *I* is expressed, which satisfies the Arrhenius equation as follows [40,43–45]:

$$D(T) = \frac{\lambda a^2}{2Z} I \tag{1}$$

where  $\lambda$  ( $\lambda$  = 2), Z (Z = 1) and a are the number of directions for atomic transitions, the dimension of diffusion and the corresponding atomic distance of diffusion, respectively.

Here, the jump frequency for both diffusions in solid-state was established using the classical transition state theory (TST) [46,47]:

$$I = vexp^{\left(-\frac{Q}{\kappa T}\right)} \tag{2}$$

where  $\nu$ , Q, T and  $\kappa$  are the effective frequencies associated with the vibration of the transition atom, the diffusion activation energy, the special temperature and the Boltzmann constant, respectively.

According to Winter–Zener theory (WZT), the  $\nu$  can be approximately expressed as [48]:

$$\nu = \left(\frac{2E_{Diff}}{ma^2}\right)^{\frac{1}{2}} \tag{3}$$

where *m* represents the atomic mass of transition atoms. Herein, two types of diffusion activation energies *Q* corresponding to self  $D_0$  and impurity  $D_s$  diffusion coefficients are gained using first principles calculations. The *Q* for self-diffusion contains two separate energies: vacancy formation energy  $E_{vac}$  and the migration energy of *Al* atom  $E_m$  in *Al* matrix. For impurity diffusion activation energy, the activation energy *Q* consists of three parts: the substitutional solution energy  $E_s$  of a *TM* atom replacing a *Al* atom, vacancy formation energy  $E_f$  in the presence of *TM* in  $Al_{107}TM$  supercell, and the migration energy of diffusion  $E_m$  [49]:

$$E_s = E_{Al_{107}TM} - 107E_{Al} - E_{TM} \tag{4}$$

$$E_f = E_{(Al_{106}TM:Vac)} - E_{Al_{107}TM} + E_{Al}$$
(5)

$$E_b = E_s + E_f \tag{6}$$

where  $E_{TM}$  and  $E_{Al}$  are the energies of single *TM* and *Al* atoms in the stable bulk, respectively, and  $E_b$  is the binding energy of a *TM* atom substituting a vacancy in *Al* matrix.

To further investigate the physical mechanism of behaviors, the electron localized function (ELF) has been drawn using the VESTA code [50]. The ELF is defined as:

$$ELF = \frac{1}{1 + \left(\frac{D_r}{Dh_r}\right)^2} \tag{7}$$

where  $D_r$  and  $Dh_r$  are the true electron gas density and the pre-assumed uniform electron gas density, respectively.

The  $E_m$ ,  $E_b$  ( $E_{vac}$ ), Q and  $D_s$  ( $D_0$ ) for TM and Al at 300 K with available experimental and theoretical values are summarized in Table 1 [51–54]. It can be seen that errors between the present and previous values in literatures for  $E_m$ ,  $E_b$  ( $E_{vac}$ ) and  $E_{Diff}$  are within 20%, and the current value of  $E_{Diff}$  of Sc element is only ~2% larger than that of the experiment value. To visually illustrate the regularity of the variations of activation energy Q as a function of the atomic number of TM, it is further plotted in Figure 2b. The result shows that the Q increases at first and then decreases as the atomic number increases (Sc-Zn, Y-Ag, Hf-Au) in the Al matrix (except for Cr of 2.23 eV), indicating that there is a correlation between the valence electron configuration of impurity elements and the activation energy Q. Additionally, the TM elements in the fourth cycle generally have lower diffusion activation energies  $Q_s$ , ranging from 0.35 to 2.60 eV. For Mn-Co, Tc-Rh and Re-Ir, they have larger  $Q_s$  in the Al matrix, which are 2.45~2.60, 3.82~3.94 and 3.95~4.26 eV, respectively, indicating that their diffusion abilities are relatively weak in the Al matrix. Meanwhile, for Cu-Zn, Ag and Au, the activation energy Q is very low, or even negative for a Cd of -0.12 eV and an Hg of -0.30 eV, as shown in Table 1, which shows they are easier to move in the Al matrix. In the undoped-Al system, self-diffusion activation energies  $Q_0$  is lower compared to all  $Q_s$  in the doped system, except for the  $Q_s$  of Cu, Zn, Y and Ag, indicating that the diffusion of most TM atoms is more difficult than self-diffusion.

The variation in activation energy Q with the temperature increasing can be calculated from the above results by combining them with the quasi-harmonic vibration (QHA) [55]; by doing this, the change in diffusion rate D with the temperature can be obtained via Equations (1)–(3), and the results are summarized in Table 1 and Figure 2c,d. It should be noted that only the self-diffusion rate  $D_0$  as a function of Q is presented in the inlet of Figure 2c, owing to the fact that all activation energies Q of TM elements are nearly the same. The self-diffusion rate  $D_0$  of  $3.55 \times 10^{-28} \text{ m}^2 \cdot \text{s}^{-1}$  for Al in this work is in general agreement with the experimental extension values from  $1.76 \times 10^{-27} \sim 4.42 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ in the range of 300~1000 K and  $1.47 \times 10^{-14}$ ~ $1.36 \times 10^{-12}$  in the range of 739~917 K in literature [56,57], seen from Table 1 and Figure 2c. Meanwhile, the theoretical predicted  $D_0$ of  $3.55 \times 10^{-28}$  m<sup>2</sup>·s<sup>-1</sup> of Al is lower than that of the experiment at 300 K. The reason for this may be that it is difficult to accurately determine the  $D_0$  due to the influence of crystal structure defects, dislocations and grain boundaries in experiments. The  $D_s$  of all impurity atoms except for Cd and Hg increases logarithmically with the increase in temperature. A negative Q for Cd and Hg cases makes it impossible to theoretically calculate values according to Equations (1) and (2). Reasonably, the D indicate the inverse pattern to Q; higher barriers mean slower passage. Additionally, the larger the value at 300 K, the lower the increasing rate. This trend result is consistent with the variation trend of  $D_s$  for Mg, Si and Cu with temperature calculated by Mantina et al. [44]. Figure 2d further shows the diffusion rate  $D_s$  at 300 K as a function of the atomic number of TM, and it can be seen that the diffusion rate  $D_s$  first decreases linearly from 2.05  $\times$  10<sup>-37</sup>, 6.47  $\times$  10<sup>-24</sup> and  $2.79 \times 10^{-44}$  m<sup>2</sup>·s<sup>-1</sup> for Sc, Y and Hf to  $2.43 \times 10^{-50}$ ,  $6.77 \times 10^{-73}$  and  $1.60 \times 10^{-78}$  m<sup>2</sup>·s<sup>-1</sup> for Mn, Ru and Ir and then increases with the increase in atomic number to  $3.09 \times 10^{-13}$ ,  $9.17 \times 10^{-17}$  and  $2.93 \times 10^{-29}$  m<sup>2</sup>·s<sup>-1</sup> for Zn, Ag and Au, respectively (except for Cr of  $3.36 \times 10^{-44} \text{ m}^2 \cdot \text{s}^{-1}$ ).

From the above results, it can be seen that higher peaks occur for half- or near half-full d shells for all cycles considered. The reason for this may be that half- or near half-full d shells of the TM element in the Al matrix are more stable and more energy is required to force them to move from the stable site to the vacancy. Although the atomic diffusion barrier changes similarly with the increase in atomic number in the same period, TM with 3d shells present a faster diffusion behavior. To explore the underlying potential, the ELF of Sc and Ru doping systems on the (010) plane are presented in Figure 2e,f. The value of ELF, which is selected as 0 to 1, demonstrates the probability of finding an electron in the neighborhood space. To be specific, when it equals 0, it reflects a strongly delocalized electron area; when it equals 1, it corresponds to a strongly localized electron area. It can be seen that, when Sc and Ru are the first nearest neighbors of the vacancy, different values of ELF are exhibited. The Ru would make the surrounding electrons appear more likely than Sc, resulting in Ru being difficult to diffuse to the vacancy.

**Table 1.** The calculated diffusion barrier  $E_m$  (eV), vacancy–solute binding energy  $E_b$  (eV), diffusion activation energy Q (eV) and diffusion rate  $D_s$  (m<sup>2</sup>·s<sup>-1</sup>) for TM atoms in Al matrix at 300 K. It should be noted that for pure Al,  $E_b$  and  $D_s$  are in fact  $E_{vac}$  and  $D_0$ , respectively. Note: A negative activation energy Q can't meet calculating  $D_s$  according to Equations (1)–(3).

| Element | $E_m$                               | E <sub>b</sub>                      | Q  | $D_s$   |
|---------|-------------------------------------|-------------------------------------|--|---|
| Al      | 0.68<br>0.55–0.70 [54]<br>0.57 [58] | 0.63<br>0.60–0.80 [54]<br>0.63 [58] | 1.31<br>1.15–1.50 [54]<br>1.20 [58]<br>1.31 [56] | $3.55 \times 10^{-28}$<br>$1.76 \times 10^{-27}$ [56] |
| Sc      | 0.85                                | 0.97                                | 1.82 1.79 [55]                                   | $2.05	imes10^{-37}$                                   |
| Ti      | 1.43                                | 0.84                                | 2.27   | $6.04 	imes 10^{-45}$                                 |
| V       | 1.90                                | 0.42                                | 2.32   | $1.09	imes10^{-45}$                                   |
| Cr      | 2.14                                | 0.09                                | 2.23   | $3.36	imes10^{-44}$                                   |

| Element | $E_m$ | $E_b$ | Q     | $D_s$                 |
|---------|-------|-------|-------|-----------------------|
| Mn      | 2.11  | 0.49  | 2.60  | $2.43	imes10^{-50}$   |
| Fe      | 1.90  | 0.63  | 2.53  | $3.10	imes10^{-49}$   |
| Со      | 1.55  | 0.90  | 2.45  | $7.79	imes10^{-48}$   |
| Ni      | 1.06  | 0.97  | 2.03  | $6.44	imes10^{-41}$   |
| Cu      | 0.57  | 0.22  | 0.79  | $2.94	imes10^{-20}$   |
| Zn      | 0.40  | -0.04 | 0.35  | $3.09	imes10^{-13}$   |
| Y       | 0.36  | 0.63  | 0.99  | $6.47 	imes 10^{-24}$ |
| Zr      | 1.19  | 0.98  | 2.17  | $2.16	imes10^{-43}$   |
| Nb      | 1.88  | 0.75  | 2.63  | $4.94	imes10^{-51}$   |
| Мо      | 2.46  | 0.75  | 3.22  | $7.40	imes10^{-61}$   |
| Tc      | 2.54  | 1.27  | 3.82  | $7.25 	imes 10^{-71}$ |
| Ru      | 2.25  | 1.69  | 3.94  | $6.77	imes10^{-73}$   |
| Rh      | 1.68  | 2.16  | 3.84  | $2.81	imes10^{-71}$   |
| Pd      | 0.98  | 1.71  | 2.68  | $5.51 	imes 10^{-52}$ |
| Ag      | 0.51  | 0.06  | 0.56  | $9.17	imes10^{-17}$   |
| Cď      | 0.35  | -0.46 | -0.12 | -                     |
| Hf      | 1.41  | 0.80  | 2.21  | $2.79	imes10^{-44}$   |
| Ta      | 2.10  | 0.41  | 2.51  | $2.90	imes10^{-49}$   |
| W       | 2.85  | 0.17  | 3.02  | $9.43	imes10^{-58}$   |
| Re      | 3.09  | 0.86  | 3.95  | $2.93	imes10^{-73}$   |
| Os      | 2.77  | 1.36  | 4.14  | $1.96	imes10^{-76}$   |
| Ir      | 2.15  | 2.11  | 4.26  | $1.60	imes10^{-78}$   |
| Pt      | 1.27  | 2.15  | 3.42  | $1.77 	imes 10^{-64}$ |
| Au      | 0.53  | 0.78  | 1.31  | $2.93	imes10^{-29}$   |
| Hg      | 0.21  | -0.50 | -0.30 | -                     |

Table 1. Cont.

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**Figure 2.** (a) The diffusion model. (b) The calculated diffusion barrier of a vacancy  $E_m$ , vacancy solute binding energy  $E_b$  (vacancy formation energy  $E_{vac}$  for self-diffusion in Al matrix) and diffusion activation energy  $E_{Diff}$  with the change in atomic number. (c) The diffusion rate D and  $E_{Diff}$  as a function of temperature. (d) The impurity diffusion rate  $D_s$  as a function of the atomic number of TM. (a,b) represent the experimental values from Murphy et al. [57] and Volin et al. [56], respectively. (e,f) The ELFs on the (010) planes of Sc and Ru doping systems, respectively.

# 3.2. Nucleation

According to the classical nucleation method (CNT) [44,56,57], the total energy of the nucleation process of second phases can be expressed as follows:  $\Delta G_{tot} = \frac{4}{3}\pi R^3 (\Delta G_V + \Delta E_{CS}) + 4\pi R^2 \gamma_{\alpha/\beta}$ . Here, a positive strain energy contribution would be a hindrance when Al<sub>3</sub>TM grains gradually form, while the difference in free energy in bulk between the matrix and particles and the interfacial free energy would promote particle nucleation.

Here, to calculate interface energy  $\gamma_{\alpha/\beta}$ , we adopt a total energy of interface model that subtracts the total energy of the phases on either side of the interface in a two-phase system [23]:

$$\gamma_{\alpha/\beta} = \frac{E_{\alpha/\beta} - (E_{\alpha} + E_{\beta})}{2A} \tag{8}$$

where *A* is the area of the interface,  $E_{\alpha/\beta}$  is the total internal energy of the relaxed  $\alpha/\beta$  system containing an interface and  $E_{\alpha}$  and  $E_{\beta}$  are the total internal energies of phases  $\alpha$  and  $\beta$  from the strains of all directions, respectively.

The chemical formation energy difference  $\Delta G_V$  of L1<sub>2</sub>-Al<sub>3</sub>TM precipitates can be expressed in dilute solid solution based thermodynamics,  $Al_nTM \rightarrow Al_3TM + Al_{n-3}$ . It can be shown as [15]

$$\Delta G_V = \Delta G_{Al_3TM} + (n-3)\Delta G_{Al} - \Delta G_{Al_nTM}$$
(9)

where n (n = 31) and  $\Delta G$  are the number of atoms and Gibbs free energy, respectively. To investigate the dependence of  $\Delta G_V$  on temperature, the non-equilibrium free energy  $\Delta G_V$  is derived as the following equation [15,59]:

$$G(V, P, T) = \min[F(V, T)] + PV$$
(10)

where F(V; T) is the free energy computed by the sum of electronic internal energy and phonon Helmholtz free energy  $F(V, T) = U_{el} + F_{vib}$ . *P* is the circumstance pressure.

Due to lattice mismatch, both the harmonic and non-harmonic contributions were observed to calculate the strain energy  $\Delta E_{CS}$  of the L1<sub>2</sub> precipitation phases [15]:

$$\Delta E_{CS}\left(x,\hat{G}\right) = \min_{a_s}\left(x\Delta E_{\alpha}^{eqi}\left(a_s,\hat{G}\right) + (1-x)\Delta E_{\beta}^{eqi}\left(a_s,\hat{G}\right)\right)$$
(11)

where  $a_s$  is the constrained superlattice parameter,  $\ddot{G}$  is the direction and x is the mole fraction of phase  $\alpha$ .  $\Delta E_{\alpha}^{eqi}$  and  $\Delta E_{\beta}^{eqi}$  are the epitaxial deformation energies of phases  $\alpha$  and  $\beta$ , respectively.

Figure 3a shows the interface model for calculating the interface properties in this work. The Al matrixes are highlighted in dashed rectangles, and different layer numbers are used for the calculation convenience. Comparing the present results with references [15,23] listed in Table 2, there are larger errors compared by Mao and Li et al. [15,23], and these errors are further discussed. The main reasons are as follows:

1. Li et al. [23] adopted the vacuum slab model for the calculation, resulting in the values of interface energies being affected by different terminal surfaces, and the interface energy of Al/Al<sub>3</sub>Ti of 61.85 mJ·m<sup>-2</sup> calculated by the vacuum model is in a good agreement with that of Li et al. according to  $\gamma_{\alpha/\beta} = \frac{E_{\alpha/\beta}^* - (E_{slab,\alpha} + E_{slab,\beta})}{S} + E_{sur}^{\alpha} + E_{sur}^{\beta}$ , where  $E_{\alpha/\beta}^*$  is the total energy of the vacuum slab model system,  $E_{slab}$  denotes the

total energy of the fully relaxed surface slabs and  $E_{sur}^{\alpha}$  and  $E_{sur}^{\beta}$  represent the surface energies of the  $\alpha$  and  $\beta$  surface slabs, respectively. Meanwhile, the strain energy caused by lattice mismatch in the vacuum slab model was not taken into account in the above equation.

2. Mao et al. [15] had investigated interface properties in a periodic supercell and, considering the strain energy of interface model, they calculated interface properties with less accuracy, performed on a 0.13 (1/Å) spacing Monkhorst–Pack k-point mesh and an energy cutoff of 300 eV.



**Figure 3.** (a) The interface models. (b–d) The calculated interface energy  $\gamma_{\alpha/\beta}$  and (e–g) strain energy  $\Delta E_{cs}$  with the change in atomic number. (h) The chemical formation energy  $\Delta G_V$  with the change in temperature. (i,j) The chemical formation energy  $\Delta G_V$  as a function of atomic number under different constant temperature conditions. (a) represent the calculated result of Li et al. [23].

| Dir.                  | (001)   |                   | (110)   |                 | (111)   |                 |
|-----------------------|---|-------------------|---|-----------------|---|-----------------|
| Systems               | γα/β  | $\Delta E_{CS}$   | γα/β  | $\Delta E_{CS}$ | γα/β  | $\Delta E_{CS}$ |
| Al/Al <sub>3</sub> Sc | 108.65<br>108.00 [15]<br>165.00 [23]<br>176.00 [23] | 0.32<br>0.60 [23] | 194.41<br>159.00 [15]<br>178.00 [15]<br>193.00 [23] | 1.50            | 204.81<br>191.00 [23]<br>189.00 [15]<br>203.00 [15] | 1.52            |
| Al/Al <sub>3</sub> Ti | -38.48<br>61.85 *<br>52.00 [23]                     | 0.20<br>0.30 [15] | -38.90<br>61.00                                     | 1.12            | 66.67<br>79.00 [15]                                 | 1.36            |
| Al/Al <sub>3</sub> V  | -147.83   | 1.77              | -203.77   | 5.10            | -75.76  | 7.56            |
| Al/Al <sub>3</sub> Cr | -270.04   | 1.52              | -379.95   | 9.92            | -167.43   | 23.16           |
| Al/Al <sub>3</sub> Mn | -468.86   | -0.14             | -429.65   | 13.80           | -225.66   | 28.62           |
| Al/Al <sub>3</sub> Fe | -291.22   | 10.64             | -283.37   | 16.58           | -113.54   | 23.69           |
| Al/Al <sub>3</sub> Co | -200.04   | 12.06             | -205.31   | 14.01           | -49.49  | 22.43           |
| Al/Al <sub>3</sub> Ni | -195.59   | 5.83              | -176.89   | 6.20            | -109.50   | 15.46           |
| Al/Al <sub>3</sub> Cu | -143.59   | 0.59              | -108.27   | 2.40            | -48.53  | 8.43            |
| Al/Al <sub>3</sub> Zn | -53.81  | 0.64              | -88.33  | 0.67            | -33.48  | 0.24            |
| Al/Al <sub>3</sub> Y  | 93.37   | 5.13              | 159.60  | 9.72            | 181.29  | 14.30           |
| Al/Al <sub>3</sub> Zr | 20.15   | 0.65              | 1.39  | 2.43            | 86.32   | 2.48            |
| Al/Al <sub>3</sub> Nb | -143.96   | 1.48              | -160.59   | 2.07            | -109.57   | 0.56            |
| Al/Al <sub>3</sub> Mo | -309.65   | 1.87              | -319.59   | 1.20            | -201.04   | 18.33           |
| Al/Al <sub>3</sub> Tc | -699.48   | -14.84            | -516.46   | 7.24            | -201.10   | 20.79           |
| Al/Al <sub>3</sub> Ru | -173.70   | 3.92              | -228.40   | 8.52            | -82.71  | 12.26           |
| Al/Al <sub>3</sub> Rh | -138.07   | 2.92              | -197.66   | 6.71            | -42.72  | 9.98            |
| Al/Al <sub>3</sub> Pd | -132.75   | 1.53              | -153.88   | 1.94            | -60.52  | 1.79            |
| Al/Al3Ag              | -142.47   | 0.86              | -46.85  | 1.31            | -5.67   | 0.40            |
| Al/Al <sub>3</sub> Cd | -75.68  | 0.51              | -261.59   | 4.33            | -55.69  | 9.33            |
| Al/Al <sub>3</sub> Hf | -37.53  | 1.14              | -25.31  | 1.79            | 69.41   | 1.59            |
| Al/Al <sub>3</sub> Ta | -169.68   | 0.50              | -198.59   | 1.36            | -124.38   | 1.26            |
| Al/Al <sub>3</sub> W  | -232.18   | 0.29              | -467.97   | 4.35            | -276.16   | 4.24            |
| Al/Al <sub>3</sub> Re | -146.35   | 4.59              | -1242.00  | 26.49           | -396.57   | 33.54           |
| Al/Al <sub>3</sub> Os | -243.80   | 4.34              | -328.80   | 8.72            | -174.06   | 13.36           |
| Al/Al <sub>3</sub> Ir | -87.86  | 3.71              | -173.40   | 6.26            | -3.44   | 10.60           |
| Al/Al <sub>3</sub> Pt | -190.37   | 0.38              | -734.31   | 2.90            | -246.39   | 17.81           |
| Al/Al <sub>3</sub> Au | -118.52   | 0.58              | -80.77  | 1.02            | -33.30  | 0.67            |
| Al/Al <sub>3</sub> Hg | -93.95  | 0.94              | -341.48   | 3.64            | -251.40   | 24.04           |

**Table 2.** The calculated interface energy  $\gamma_{\alpha/\beta}$  (mJ·m<sup>-2</sup>) and strain energy  $\Delta E_{cs}$  (meV·atom<sup>-1</sup>) in Al/Al<sub>3</sub>TM interface systems. (Note: A \* symbol represents the calculated result from the vacuum slab model).

The calculated  $\gamma_{\alpha/\beta}$  with the increase in atomic number is further depicted in Figure 3b–d. According to the CNT, the theoretical nucleation radius R<sup>\*</sup> cannot be calculated by a negative  $\gamma_{\alpha/\beta}$ , and the  $\gamma_{\alpha/\beta}$  of all Al/Al<sub>3</sub>TM are less than 0 mJ·m<sup>-2</sup>, except for the (111) of Al/Al<sub>3</sub>Sc, Al/Al<sub>3</sub>Ti, Al/Al<sub>3</sub>(Y-Zr) and Al<sub>3</sub>Hf systems.

It can be seen from Figure 3b,c that the  $\gamma_{\alpha/\beta}$  of Al/Al<sub>3</sub>TM (TM = (Sc-Zn, Y-Cd)) decreases from Sc and Y to Mn and Tc, and then increases to Zn and Cd, respectively, except for the (001) of Al/Al<sub>3</sub>(Fe-Co), the (111) of Al/Al<sub>3</sub>Pd and the (110) and (111) of Al/Al<sub>3</sub>Cd. These trends of  $\gamma_{\alpha/\beta}$  for Al/Al<sub>3</sub>TM (TM = (H<sub>f</sub>-Hg)) in the (110) and (111) systems present two Al/Al<sub>3</sub>Re and Al/Al<sub>3</sub>Pt compound troughs in Figure 3d, and they show the same change with the increase in atomic number. For the (001) system, the  $\gamma_{\alpha/\beta}$  of Al/Al<sub>3</sub>TM (TM = (H<sub>f</sub>-Hg) is larger than  $-250 \text{ mJ} \cdot \text{m}^{-2}$ , and the Al/Al<sub>3</sub>TM with 3d<sup>6</sup>4s<sup>2</sup> has the lowest  $\gamma_{\alpha/\beta}$ . Figure 3e shows the variation of strain energy  $\Delta E_{cs}$  of Al/Al<sub>3</sub>TM (TM = (Sc-Zn) with the increase in atomic number. It can be seen that the  $\Delta E_{cs}$  increases from 0.32~1.52 meV·atom<sup>-1</sup> for Sc to 12.06 meV·atom<sup>-1</sup> for Co on the (001) system, to 16.58 meV·atom<sup>-1</sup> for Fe on the (110) system, and to 28.62 meV·atom<sup>-1</sup> for Mn on the (111) system, respectively, and then they all decrease to 0.24 ~ 0.67 meV·atom<sup>-1</sup> for Zn (except for Al/Al<sub>3</sub>Mn, of the order of  $-0.14 \text{ meV·atom}^{-1}$ ). For the (110) and (111) systems

of Al/Al<sub>3</sub>TM (TM = (Y-Cd, Hf-Hg)), as seen in Figure 3f,g, respectively, the largest values of  $\Delta E_{cs}$  for the (110) and (111) interface systems are all located at Al/Al<sub>3</sub>Re, being 26.49 and 33.54 meV·atom<sup>-1</sup>, respectively, while the (001) interface system of Al/Al<sub>3</sub>Tc has the lowest value of  $\Delta E_{cs}$ , being -14.84 meV·atom<sup>-1</sup>.

The trends of  $\Delta G_V$  as a function of temperature for all Al<sub>3</sub>TM compounds have been calculated according to Equations (10) and (11), and results are shown as Figure 3h. The results show that the  $\Delta G_V$  of all Al<sub>3</sub>TM change slightly in the temperature range of 0~1000 K, except that the  $\Delta G_V$  of Al<sub>3</sub>Sc, Al<sub>3</sub>Cu, Al<sub>3</sub>(Y-Zr), Al<sub>3</sub>Cd, Al<sub>3</sub>Hf and Al<sub>3</sub>Hg increase nonlinearly from -89.69, -1.44, -130.51, -93.86, -1.65, -72.35, and 0.65 meV·atom<sup>-1</sup> to -24.38, 66.09, -88.46, -44.47, 71.60, -2.05 and ~88.51 meV·atom<sup>-1</sup>, respectively. Furthermore, the obtained  $\Delta G_V$  as a function of the atomic number of TM is shown in Figure 3i,j, and the calculated values of -66.46 and -61.54 meV·atom<sup>-1</sup> for Al<sub>3</sub>Sc and Al<sub>3</sub>Ti, respectively, at 600 K agree well with the value of  $-61.14 \text{ meV} \cdot \text{atom}^{-1}$  at 350 °C (623 K) for Al<sub>3</sub>Sc and  $-66.15 \text{ meV} \cdot \text{atom}^{-1}$  at 300 (573 K) for Al<sub>3</sub>Ti calculated by Li et al. [15]. From Figure 3i, one can see that the  $\Delta G_V$  at 300 K increases from -80.96 meV atom<sup>-1</sup> for Sc,  $-120.46 \text{ meV} \cdot \text{atom}^{-1}$  for Y and  $-66.82 \text{ meV} \cdot \text{atom}^{-1}$  for Hf to 20.37 meV \cdot \text{atom}^{-1} for Mn, 53.89 meV·atom<sup>-1</sup> for Tc and 74.50 meV·atom<sup>-1</sup> for Re, and then decreases slightly to -11.72 meV·atom<sup>-1</sup> for Co, 9.62 meV·atom<sup>-1</sup> for Rh and 4.89 meV·atom<sup>-1</sup> for Ir, respectively. As a final step, they change slightly. At 600 K, the variation trends of  $\Delta G_V$  for 3–5d TMs are the same as those at 300 K.

# 3.3. Surface Energy

In the framework of Peierls theory, a lower surface energy of bulk materials in comparison to an unstable stacking fault will cause metals to crack from material failure [42,60]. Thus, it is necessary to analyze surface energy for all Al<sub>3</sub>TM particles and the Al matrix. The surface energy of Al is given by the following formula [61,62]:

$$E_{sur} = \frac{E_{Al}^{slab} - N\mu_{Al}^{bulk}}{2A} \tag{12}$$

where  $E_{Al}^{slab}$  and N are the total energy and the number of Al atoms in the slab model, respectively.  $\mu_{Al}^{bulk}$  represents the chemical potential of a single atom in bulk Al.

For stoichiometric surfaces (111) of the Al<sub>3</sub>TM slab, the calculated formula is given as follows:

$$3\mu_{Al}^{slab} + \mu_{TM}^{slab} = \mu_{Al_3TM}^{bulk} \tag{13}$$

$$E_{sur} = \frac{E_{Al_3TM}^{slab} - N\mu_{Al_3TM}^{bulk}}{2A}$$
(14)

where  $\mu_{Al}^{slab}$ ,  $\mu_{TM}^{slab}$  and  $\mu_{Al_3TM}^{bulk}$  are the chemical potential of Al, AlTM-terminated and Al<sub>3</sub>TM bulk, respectively. *N* and *A* are the number of Al<sub>3</sub>TM cells and the surface area, respectively.

To further discuss the non-stoichiometric (001) and (110) surfaces of the Al3TM (3NTM  $\neq$  NAl), we used the following the equation [24,63]:

$$E_{sur} = \frac{E_{Al_3TM}^{slab} - N\mu_{Al_3TM}^{bulk} + n\mu_{Al}^{slab}}{2A}$$
(15)

where *n* is the number of the rest (n < 0) and missing (n > 0) Al atoms.

To obtain  $\mu_{Al}^{slab}$  in the systems, we first need to avoid Al and Sc bulk phases. Therefore,  $\mu_{Al}^{slab}$  and  $\mu_{Sc}^{slab}$  are limited, as follows:

$$\mu_{Al}^{slab} - \mu_{Al}^{bulk} < 0 \tag{16}$$

$$\mu_{TM}^{slab} - \mu_{TM}^{bulk} < 0 \tag{17}$$

Further, the thermodynamic stability of AITM compounds should meet the equation given by:

$$3\mu_{Al}^{bulk} + \mu_{TM}^{bulk} + \Delta H_f = \mu_{Al_3TM}^{bulk}$$
(18)

Combined with Equations (12) and (15)–(17), two limit values of  $\mu_{Al}^{slab}$  are respectively given by:

$$\mu_{Al}^a = \mu_{Al}^{slab} = \mu_{Al}^{bulk} \tag{19}$$

$$\mu_{Al}^{b} = \mu_{Al}^{slab} = \mu_{Al}^{bulk} + \frac{1}{3}\Delta H_f$$
(20)

The calculated surface energies of AlTM from different Al chemical potentials,  $\mu_{Al}^a$  and  $\mu_{Al}^b$ , are summarized in Table 3 as references. To solve the dependence of surface energy on Al chemical potential, the average surface energy of non-stoichiometric surfaces is obtained by two identical index surfaces of different termination [24,63]:

$$E_{sur}^{ave} = \frac{1}{4A} \left[ E_{slab}^{Al} + E_{slab}^{AlTM} - \left( N_{slab}^{Al} + N_{slab}^{AlTM} \right) \times \mu_{Al_3TM}^{bulk} \right]$$
(21)

where  $E_{slab}^{Al}$ ,  $N_{slab}^{Al}$  and  $E_{slab}^{AlTM}$ ,  $N_{slab}^{AlTM}$  are the relaxed energy and total number of *TM* atoms in Al and AlTM-terminated surfaces, respectively.

**Table 3.** The calculated surface energy  $E_{sur}$  (J·m<sup>-2</sup>) of the (001) and (110) surfaces from different Al chemical potential  $\mu_{Al}^a$  and  $\mu_{Al}^b$  in Al<sub>3</sub>TM.

|                    | (001)        |                  |              | (110)        |              |              |              |              |
|--------------------|--------------|------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Systems            | Al-          | l-Ter. AlTM-Ter. |              | -Ter.        | Al-Ter.      |              | AlTM-Ter.    |              |
| -                  | $\mu^a_{Al}$ | $\mu^b_{Al}$     | $\mu^a_{Al}$ | $\mu^b_{Al}$ | $\mu^a_{Al}$ | $\mu^b_{Al}$ | $\mu^a_{Al}$ | $\mu^b_{Al}$ |
| Al <sub>3</sub> Sc | 1.10         | 1.69             | 1.42         | 0.84         | 1.19         | 1.61         | 1.63         | 1.22         |
| Al <sub>3</sub> Ti | 1.04         | 1.53             | 1.70         | 1.21         | 0.99         | 1.34         | 1.84         | 1.49         |
| Al <sub>3</sub> V  | 1.03         | 1.24             | 1.61         | 1.40         | 0.86         | 1.01         | 1.77         | 1.63         |
| Al <sub>3</sub> Cr | 0.97         | 0.92             | 1.54         | 1.59         | 0.63         | 0.60         | 1.50         | 1.53         |
| Al <sub>3</sub> Mn | 0.93         | 0.99             | 1.55         | 1.49         | 0.42         | 0.47         | 1.19         | 1.14         |
| Al <sub>3</sub> Fe | 1.06         | 1.23             | 1.57         | 1.39         | 0.78         | 0.90         | 1.51         | 1.39         |
| Al <sub>3</sub> Co | 0.97         | 1.29             | 1.32         | 0.99         | 0.77         | 0.99         | 1.32         | 1.09         |
| Al <sub>3</sub> Ni | 0.78         | 1.10             | 1.03         | 0.71         | 0.73         | 0.96         | 0.90         | 0.68         |
| Al <sub>3</sub> Cu | 0.83         | 0.89             | 0.99         | 0.92         | 0.87         | 0.92         | 0.85         | 0.80         |
| Al <sub>3</sub> Zn | 0.84         | 0.82             | 0.78         | 0.80         | 0.93         | 0.91         | 0.75         | 0.77         |
| Al <sub>3</sub> Y  | 1.13         | 1.63             | 0.96         | 0.46         | 1.12         | 1.47         | 1.34         | 0.98         |
| Al <sub>3</sub> Zr | 0.88         | 1.46             | 1.36         | 0.77         | 0.88         | 1.29         | 1.59         | 1.18         |
| Al <sub>3</sub> Nb | 0.81         | 1.16             | 1.32         | 0.97         | 0.70         | 0.95         | 1.61         | 1.37         |
| Al <sub>3</sub> Mo | 0.36         | 0.51             | 0.88         | 0.73         | 0.26         | 0.36         | 1.17         | 1.08         |
| Al <sub>3</sub> Tc | 1.02         | 1.29             | 1.62         | 1.35         | 0.00         | 0.18         | 0.77         | 0.59         |
| Al <sub>3</sub> Ru | 1.17         | 1.67             | 1.62         | 1.11         | 0.80         | 1.15         | 1.53         | 1.18         |
| Al <sub>3</sub> Rh | 0.85         | 1.54             | 1.01         | 0.31         | 0.66         | 1.15         | 1.04         | 0.55         |
| Al <sub>3</sub> Pd | 0.58         | 1.05             | 0.67         | 0.20         | 0.44         | 0.80         | 0.47         | 0.12         |
| Al <sub>3</sub> Ag | 0.68         | 0.63             | 0.53         | 0.58         | 0.72         | 0.68         | 0.50         | 0.53         |
| Al <sub>3</sub> Cd | 0.81         | 0.63             | 0.23         | 0.41         | 0.72         | 0.60         | 0.40         | 0.53         |
| Al <sub>3</sub> Hf | 0.96         | 1.45             | 1.63         | 1.14         | 0.94         | 1.29         | 1.78         | 1.43         |
| Al <sub>3</sub> Ta | 0.91         | 1.10             | 1.66         | 1.46         | 0.75         | 0.89         | 1.82         | 1.68         |
| Al <sub>3</sub> W  | 0.64         | 0.54             | 1.45         | 1.54         | 0.57         | 0.50         | 1.50         | 1.56         |
| Al <sub>3</sub> Re | 0.90         | 0.95             | 1.76         | 1.70         | 0.00         | 0.04         | 0.93         | 0.89         |
| Al <sub>3</sub> Os | 1.08         | 1.40             | 1.81         | 1.49         | 0.59         | 0.82         | 1.52         | 1.29         |
| Al <sub>3</sub> Ir | 1.07         | 1.75             | 1.38         | 0.69         | 0.77         | 1.26         | 1.39         | 0.91         |
| Al <sub>3</sub> Pt | 0.66         | 1.30             | 0.71         | 0.07         | 0.49         | 0.97         | 0.55         | 0.08         |
| Al <sub>3</sub> Au | 0.55         | 0.70             | 0.35         | 0.20         | 0.46         | 0.57         | 0.31         | 0.20         |
| Al <sub>3</sub> Hg | 0.67         | 0.45             | -0.15        | 0.07         | 0.35         | 0.20         | 0.19         | 0.34         |

Figure 4a shows the slab model for calculating  $E_{sur}$ , and the detail calculated results of  $E_{sur}^{ave}$  of Al<sub>3</sub>TM (RE = Sc-Zn, Y-Cd and Hf-Hg) are depicted in Table 4. It can be seen that for pure Al, Al<sub>3</sub>(Sc-V) and Al<sub>3</sub>(Y-Nb), the calculated values of this work are in good agreement with references [24,64,65]. The  $E_{sur}^{ave}$  of low index surfaces of cubic Al follows in the sequence of (110) > (100) > (111), which follows the general law of surface energies for face-centered cubic metals [66]. Figure 4c–e illustrates the change in  $E_{sur}^{ave}$  with the atomic number of TM elements, and it can be found that the variation tendency of  $E_{sur}^{ave}$  of Al<sub>3</sub>TM intermetallic compounds presents similar characteristics for different cycles. For example, the  $E_{sur}^{ave}$  of Al<sub>3</sub>TM for 3d elements firstly decreases from Sc to Mn, and then increases to Fe, and then decreases to Ni, and finally changes slightly in the (001) surface. The variation ranges of  $E_{sur}^{ave}$  for the (001), (110) and (111) surfaces of Al<sub>3</sub>TM are 0.25~1.44, 0.26~1.45 and  $-0.32 \sim 1.18 \text{ J} \cdot \text{m}^{-2}$ , respectively, and the (111) surface has the lowest surface energy for all elements. As can be seen from Figure 4e,f, we have calculated the values of ELF by using the Equation (7) on the (111) plane of  $Al_3Sc$  and  $Al_3Mo$ . It can be seen that the (111) plane of Al<sub>3</sub>Sc has more strongly localized electron areas than the (111) plane of Al<sub>3</sub>Mo, indicating that strongly localized electrons make the surface energy lower. Clearly, if the  $E_{sur}^{ave}$  of Al<sub>3</sub>TM is larger than that of Al, they would increase the toughness of Al alloys such as Al<sub>3</sub>Sc. However, the complete toughness is not only determined by the above results but also by assessing the information of generalized stacking fault energy (GSFE) for particles in the Al matrix. The work needed for this is underway and will be published elsewhere.

**Table 4.** The calculated surface energy  $E_{sur}$  (J·m<sup>-2</sup>) in Al or Al<sub>3</sub>TM.

| Systems            | (001)           | (110)           | (111)                      |
|--------------------|-----------------|-----------------|----------------------------|
| Al                 | 0.79; 0.93 [23] | 0.87; 0.98 [23] | 0.68; 0.73 [39] 0.81 [23]  |
| Al <sub>3</sub> Sc | 1.26; 1.32 [24] | 1.41; 1.45 [24] | 1.18; 1.22 [24]; 1.17 [39] |
| Al <sub>3</sub> Ti | 1.37            | 1.42            | 0.92; 0.93 [39]            |
| Al <sub>3</sub> V  | 1.32            | 1.32            | 0.72; 0.65 [39]            |
| Al <sub>3</sub> Cr | 1.25            | 1.07            | 0.33                       |
| Al <sub>3</sub> Mn | 1.24            | 0.81            | 0.33                       |
| Al <sub>3</sub> Fe | 1.31            | 1.15            | 0.56                       |
| Al <sub>3</sub> Co | 1.14            | 1.04            | 0.67                       |
| Al <sub>3</sub> Ni | 0.91            | 0.82            | 0.57                       |
| Al <sub>3</sub> Cu | 0.91            | 0.86            | 0.69                       |
| Al <sub>3</sub> Zn | 0.81            | 0.84            | 0.73                       |
| Al <sub>3</sub> Y  | 1.05            | 1.23            | 1.06; 1.11 [39]            |
| Al <sub>3</sub> Zr | 1.12            | 1.23            | 0.80; 0.94 [39]            |
| Al <sub>3</sub> Nb | 1.06            | 1.16            | 0.54; 0.59 [39]            |
| Al <sub>3</sub> Mo | 0.62            | 0.73            | -0.32                      |
| Al <sub>3</sub> Tc | 1.32            | 0.39            | -0.22                      |
| Al <sub>3</sub> Ru | 1.39            | 1.17            | 0.44                       |
| Al <sub>3</sub> Rh | 0.93            | 0.85            | 0.46                       |
| Al <sub>3</sub> Pd | 0.62            | 0.46            | 0.21                       |
| Al <sub>3</sub> Ag | 0.61            | 0.61            | 0.46                       |
| Al <sub>3</sub> Cd | 0.52            | 0.56            | 0.47                       |
| Al <sub>3</sub> Hf | 1.30            | 1.36            | 0.87                       |
| Al <sub>3</sub> Ta | 1.28            | 1.29            | 0.66                       |
| Al <sub>3</sub> W  | 1.04            | 1.05            | 0.13                       |
| Al <sub>3</sub> Re | 1.32            | 0.46            | -0.32                      |
| Al <sub>3</sub> Os | 1.45            | 1.06            | 0.41                       |
| Al <sub>3</sub> Ir | 1.22            | 1.08            | 0.73                       |
| Al <sub>3</sub> Pt | 0.69            | 0.52            | 0.30                       |
| Al <sub>3</sub> Au | 0.45            | 0.38            | 0.35                       |
| Al <sub>3</sub> Hg | 0.26            | 0.27            | 0.27                       |

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**Figure 4.** (a) The slab model. (b–d) The calculated average surface energy  $E_{sur}^{ave}$  with the change in atomic number. (e,f) The ELF on the (111) plane of Al<sub>3</sub>Sc and Al<sub>3</sub>Mo systems, respectively.

# 4. Conclusions

In this work, we have calculated the diffusion rates of TM elements in Al and the key parameters of nucleation and growth of second phase particles  $Al_3TM$  (TM = Sc-Zn, Y-Cd and Hf-Hg) using the first principles combing with quasi-harmonic approximation in the theoretical framework of density functional theory. Firstly, as can be seen from the discussed results, the trends of the *Q*, chemical formation and surface energies with the change in atomic number in the same cycle are similar. The reason may be related to the valence electron configures (VECs) of TM elements because TM in the same cycle has the same VECs. Meanwhile, the calculation interface and strain energy of  $Al_3TM/Al$  composed of the same cycle of TM elements show a lack of similarity. The reason for this may be that the interface and strain energy are co-determined by the matrix and second phases. Here, the main conclusions are as follows:

- 1. In the vacancy–substitution model, the diffusion activation energy Q first increases, and then decreases with the increase in atomic number (Sc-Zn, Y-Ag and Hf-Au) in the Al matrix, except for Cr; the TM elements in the fourth cycle generally have lower  $Q_{s}$ .
- 2. Mn-Co, Tc-Rh and Re-Ir elements have larger activation energies  $Q_s$  in the Al matrix, while Cu-Zn, Ag and Au have lower activation energies  $Q_s$ ; even Cd and Hg elements have negative activation energies. In the undoped-Al system, the self-diffusion activation energy  $Q_0$  is lower compared to all  $Q_s$  in the doped system, except for the  $Q_s$  of Cu, Zn, Y and Ag.
- 3. The diffusion rate  $D_s$  of all impurity atoms increases logarithmically with the increase in temperature. With the increase in atomic number, the diffusion rate  $D_s$  first decreases linearly from Sc, Y and Hf to Mn, Ru and Ir, and then increases to Zn, Ag and Au for 3–5d TM elements, respectively.
- 4. With the increase in atomic number, the interface energy  $\gamma_{\alpha/\beta}$  of Al/Al<sub>3</sub>TM (TM = (Sc-Zn, Y-Cd)) decreases from Sc and Y to Mn and Tc, and then increases to Zn and

Cd, respectively, except for (001) in Al/Al<sub>3</sub>(Fe-Co), (111) in Al/Al<sub>3</sub>Pd and (110) and (111) in Al/Al<sub>3</sub>Cd. Meanwhile, the strain energy  $\Delta E_{cs}$  increases from Sc to Co in the (001) system, to Fe in the (110) system, and to Mn in the (111) system, respectively, and then they all decreases to Zn, except for Al/Al<sub>3</sub>Mn. The largest values of  $\Delta E_{cs}$  for (110) and (111) interface systems are all located at Al/Al<sub>3</sub>Re, while the (001) interface system of Al/Al<sub>3</sub>Tc has the lowest value.

- 5. The variation in chemical formation energy  $\Delta G_V$  of all Al<sub>3</sub>TM changes slightly in the temperature range of 0~1000 K, except that the  $\Delta G_V$  of Al<sub>3</sub>Sc, Al<sub>3</sub>Cu, Al<sub>3</sub>(Y-Zr), Al<sub>3</sub>Cd, Al<sub>3</sub>Hf and Al<sub>3</sub>Hg increase nonlinearly. With the increase in atomic number at 300 K, the  $\Delta G_V$  increases from Sc, Y and Hf to Mn, Tc and Re at first, and then decreases to Co, Rh and Ir, respectively, and finally, it slightly changes. The variation trends of the  $\Delta G_V$  for 3–5d TMs are the same as those at 300 K.
- 6. With the increase in atomic number, the trend of  $E_{sur}^{ave}$  of Al<sub>3</sub>TM intermetallic compounds presents a similar change in different cycles and the (111) surface always has the lowest surface energy in all surfaces of Al<sub>3</sub>TM particles.

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**Data Availability Statement:** In this article, the key parameters of growth and nucleation of Al<sub>3</sub>TM particles based on the corresponding models (see Figures 2 and 3) have been discussed in our work. Figure 4 describe calculated surface energy of Al<sub>3</sub>TM and Al. Tables 1–4 present important data as a reference. All data can be found in the manuscript.

**Conflicts of Interest:** The authors declare that they have no known competing financial interest or personal relationships that have influenced the work reported in this paper.

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