Investigation on Mg₃Sb₂/Mg₂Si Heterogeneous Nucleation Interface Using Density Functional Theory

Mingjie Wang, Guowei Zhang, Hong Xu * and Yizheng Fu

School of Materials Science and Engineering, North University of China, Shanxi 030051, China; 15513882577@163.com (M.W.); hhm727@163.com (G.Z.); wmj313999@126.com (Y.F.)

Received: 25 February 2020; Accepted: 30 March 2020; Published: 3 April 2020

Abstract: In this study, the cohesive energy, interfacial energy, electronic structure, and bonding of Mg₂Si (111)/Mg₃Sb₂ (0001) were investigated by using the first-principles method based on density functional theory. Meanwhile, the mechanism of the Mg₃Sb₂ heterogeneous nucleation potency on Mg₂Si grains was revealed. The results indicated that the Mg₃Sb₂ (0001) slab and the Mg₂Si (111) slab achieved bulk-like characteristics when the atomic layers N ≥ 11, and the work of adhesion of the hollow-site (HCP) stacking structure (the interfacial Sb atom located on top of the Si atom in the second layer of Mg₂Si) was larger than that of the other stacking structures. For the four HCP stacking structures, the Sb-terminated Mg₃Sb₂/Si-terminated Mg₂Si interface with a hollow site showed the largest work of adhesion and the smallest interfacial energy, which implied the strongest stability among 12 different interface models. In addition, the difference in the charge density and the partial density of states indicated that the electronic structure of the Si-HCP-Sb interface presented a strong covalent, and the bonding of the Si-HCP-Mg interface and the Mg-HCP-Sb interface was a mixture of a covalent bond and a metallic bond, while the Mg-HCP-Mg interfacial bonding corresponded to metallicity. As a result, the Mg₂Si was conducive to form a nucleus on the Sb-terminated-hollow-site Mg₃Sb₂ (0001) surface, and the Mg₃Sb₂ particles promoted the Mg₂Si heterogeneous nucleation, which was consistent with the experimental expectations.

Keywords: first-principles method; Heterogeneous nucleation; interfacial energy; Mg₂Si (111)/Mg₃Sb₂ (0001) interface

1. Introduction

Aluminium-magnesium-silicon alloys have shown considerable promise as the universal candidate materials for automotive and aerospace applications because of the formation of a Mg₂Si heterogeneous nucleus [1,2]. Computational simulations and experimental reports have elucidated the potency of Mg₂Si as a heterogeneous particle to reinforce α-Al and α-Mg nucleation in aluminium and magnesium alloys, respectively [3–5]. Although the Mg₂Si compound has a high hardness and elastic modulus, the coarse primary Mg₂Si phase, that has also been called Chinese script Mg₂Si in the existing literature, that appears in the Mg₂Si alloy cannot meet the requirements of engineering performance [6–8]. Thus, the heterogeneous nuclei for the refinement of the coarse Mg₂Si phase are considered the most effective method to achieve specific engineering-designed requirements [9,10]. To date, the attention has been on the grain-refining efficiency, for the Mg₂Si phase, of adding an alterant [11–15] to Mg-Si alloys. For instance, Ba₂Sb, CaSb₂, Mg₃Sb₂, Li₂Sb, and Mg₃P₂ show a positive efficiency in the grain improvement of Mg₂Si. Variations with various rare-earth elements, such as Y, La, Nd, and Gd [16–19], have been reported. Among the three common Sb-based master alloys, the lattice parameters of
antimony trimagnesium have the lowest mismatch with the Mg$_2$Si nucleation phase [20]. Therefore, it is understandable that Mg$_3$Sb$_2$ may refine the size of Mg$_2$Si.

The theoretical derivation of the interfacial properties and the interrelationships of phases at the interface based on density functional theory (DFT) has been widely used to predicate heterogeneous nucleation [21]. According to the literature, the morphology of Mg$_2$Si is inclined to transform into an octahedron shape from Chinese script Mg$_2$Si through surface anisotropy by the first-principles simulation, when Sb is doped in a Mg$_2$Si crystal [22]. Previous studies have proven that the formation of Mg$_3$(Sb, Si)$_2$ and Mg$_3$Sb$_2$ particles can act as the heterogeneous nuclei of primary Mg$_2$Si to refine the particle size of the primary Mg$_2$Si crystals [23]. However, the research on the structure and interfacial characteristics of a heterogeneous nucleation interface between the Mg$_2$Si phase and the Mg$_3$Sb$_2$ substrates has been predominantly ignored.

Recent studies have been carried out using theoretical evidence to investigate the nucleation potential of a heterogeneous substrate through research on the properties of the bulk, interface stability, and interfacial energy of a heterogeneous nucleation interface [24–26]. A first-principles calculation with the density functional theory (DFT) as an atomic analysis method has been widely implemented to illustrate heterogeneous nucleation [27,28]. Theoretical estimates of heterogeneous nucleation between two solid interfaces have been mainly based on the Bramfitt mismatch theory [29], which elucidates that the smaller the mismatch of two heterogeneous lattice structures is, the smaller the interface energy is and the more effective the heterogeneous core growth is.

In this work, the surface energy, work of adhesion, interfacial energy, and electronic properties of Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) interfaces were investigated through the density functional theory, which provides theoretical support for Mg$_3$Sb$_2$ as the heterogeneous nucleation substrates of Mg$_2$Si grains, and which lays the theoretical foundation for the grain refinement of aluminium-magnesium alloys. Because the crystal structures of Mg$_2$Si and Mg$_3$Sb$_2$ are cubic and trigonal lattices respectively, we chose to study the Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) interface. According to the equation of Bramfitt, the lattice mismatch of Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) is only 2.02%.

2. Computational Methodology

The interfacial and surface properties of Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001), such as surface energies, work of adhesion, and interfacial bonding energies, were implemented in the Cambridge serial total energy package (CASTEP) code based on the density functional theory [30,31]. To calculate the self-consistent electronic density, the generalized gradient approximation (GGA) [32,33] with PW91 functional was performed to obtain the exchange-correction function in this study. The valence electrons of Mg, Si, and Sb, calculated in terms of their pseudopotentials, were 2p$^6$3s$^2$, 3s$^2$3p$^2$, and 5s$^2$5p$^3$4d$^1$, respectively. All the plane wave cut-off energies for the bulk, surface, and interface were selected as 520 eV, the value of the k point was set as 10 × 10 × 10 for bulk Mg$_2$Si and Mg$_3$Sb$_2$, and that for their surface and interface was set to 6 × 6 × 1 and 8 × 8 × 1, respectively. The self-consistent field (SCF) convergence threshold was set as 1.0 × 10$^{-6}$ eV/atom to solve the Kohn-Sham equation, and the equilibrium crystal structure was obtained using the Broyden Fletcher Goldfrab and Shanno (BFGS) method. Moreover, the convergence tolerances for energy changes, force tolerance, stress, and displacement tolerance were set to 1.0 × 10$^{-6}$ eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.01 Å, respectively.

3. Bulk and Surface Properties

3.1. Bulk Properties of Mg$_2$Si and Mg$_3$Sb$_2$

To estimate the reliability of the computational methods, space groups, the lattice constants, bulk modulus, and elastic constants for bulk Mg$_2$Si and bulk Mg$_3$Sb$_2$, as listed in Table 1, were implemented using the density functional theory. From Table 1, the crystal structures of Mg$_2$Si and Mg$_3$Sb$_2$, as shown in Figure 1, are cubic and trigonal crystal systems with the space groups of Fm$\overline{3}$m and P$\overline{3}$m$_1$, respectively. The calculated results were in reasonable agreement with the previous theoretical calculations and
experimental data [34–37], which verified the reliability of the calculations. Moreover, to obtain further insight into the bonding types of bulk Mg$_2$Si and bulk Mg$_3$Sb$_2$, the total and partial densities of the states for bulk Mg$_2$Si and bulk Mg$_3$Sb$_2$ were investigated, as shown in Figure 2. This figure clearly shows that the major conduction band states were Mg 2p orbitals for both bulk Mg$_2$Si and bulk Mg$_3$Sb$_2$, which indicated that the metallic bonding existed in the Mg$_2$Si and Mg$_3$Sb$_2$ phase. Moreover, Figure 2a shows that from $-9.5$ eV to $-7.5$ eV, the vast majority of the valence band states were Si 3s, and that from $-4.5$ eV to the Fermi level a considerable majority of the conduction band states were Si 3p, which suggested that the bonding in the Mg$_2$Si phase included both metallic bonds and covalent bonds.

Table 1. Calculated and experimental value of the lattice constants, bulk modulus and formation energy of Mg$_2$Si and Mg$_3$Sb$_2$.

| System     | Method      | Space Group | Elastic Constants | Lattice Constants | Bulk Modulus | Formation Energy |
|------------|-------------|-------------|-------------------|-------------------|--------------|-----------------|
| Mg$_2$Si   | This work   | Fm3m        | $C_{11}$ | 13.4          | 25.3          | 47.9            | 6.365  | 6.365 | 54.3 | $-2.24$ |
|            | Other works |             | $C_{12}$ | 11.6          | 23.7          | 49.5$^{34}$    | 6.346  | 6.346 | 55.3$^{34}$ | $-2.39$ |
|            | Experiment  |             | $C_{13}$ | 13.2          | 26.3          | 48.5$^{35}$    | 6.350  | 6.350 | 57.3$^{35}$ |
| Mg$_3$Sb$_2$| This work   | P3m1        | $C_{44}$ | 41.5          | 86.7          | 48.5           | 16.1   | 18.9  | 4.592 | 7.272  | 43.1 | $-2.12$ |
|            | Other works |             | $C_{66}$ | 40.4$^{36}$  | 84.4$^{36}$  | 46.7$^{36}$    | 15.4$^{36}$ | 17.6$^{36}$ | 4.573$^{36}$ | 7.229$^{36}$ | 43.9$^{36}$ | $-2.54$ |
|            | Experiment  |             |          | 4.606$^{37}$ | 7.295$^{37}$ | 45.3$^{37}$    |        |       |       |        |       |       |

Figure 1. The crystal structure of (a) Mg$_3$Sb$_2$ and (b) Mg$_2$Si.

Figure 2. Partial density of state (DOS) charts of (a) Mg$_2$Si and (b) Mg$_3$Sb$_2$.

3.2. Surface Properties of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001)

The convergence test for the different thickness slabs of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) was significant for bulk-like interiors to ensure a sufficient thickness of the interface. Thus, the convergence tests of the Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) slabs were performed first to confirm whether the optimal number of layers was appropriate for the bulk-like interior. Commonly, the calculation accuracy of the obtained results increased with an increasing number of layers. Therefore, the selection of the number of layers, considering the cost of the computational time, applied to the convergence test.
The surface energy of the Mg-based phase variation with various terminated atoms was used as one of the important parameters to elucidate the surface stability. The calculation of surface energy can be expressed as follows [38]:

$$E_{\text{surface}} = \frac{1}{2A_{\text{surface}}} [E_{\text{slab}}(N) - NE_{\text{bulk}}]$$  \hspace{1cm} (1)

where $E_{\text{slab}}(N)$ is the total energy of the slab, $E_{\text{bulk}}$ is the bulk energy per layer of the Mg-based bulk after optimisation, $A_{\text{surface}}$ is the surface area, and $N$ is the number of surface slabs. Moreover, the odd-numbered slabs were selected to eliminate the influence of the polar surface on the computational results, and a vacuum gap (10 Å) was inserted on the surface of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) to erase the periodic effect between the surface atoms.

To further determine the thickness of both the Mg$_2$Si (111) slab and the Mg$_3$Sb$_2$ (0001) slab, different termination conditions were modelled, such as Mg-terminated and Si-terminated Mg$_2$Si (111) slabs, and Mg-terminated and Sb-terminated Mg$_3$Sb$_2$ (0001) slabs. Different numbers of layers (5, 7, 9, and 11) were considered for the convergence tests of four different terminated slabs. Therefore, the distances between two adjacent layers after the surface relaxation of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) with different terminations and slab thicknesses are presented in Table 2. This table shows that the interlayer relaxation change of both Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) slabs exhibited a converging trend when the atomic layers were $N \geq 11$. Therefore, 11-layer atoms of both Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) slabs were constructed, and a four-surface model was built, as shown in Figure 3.

Table 2. The interlayer relaxation change ($\Delta_{ij}$) convergence of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) with respect to the termination and atom layers.

| Surface        | Termination | Interlayer | Slab Thickness, N |
|----------------|-------------|------------|-------------------|
|                |             |            | 5    | 7    | 9    | 11   |
| Mg$_2$Si (111) | Mg          | $\Delta_{12}$ | −13.2 | −12.35 | 8.79 | −8.047 |
|                |             | $\Delta_{23}$ | 4.53  | 7.98   | −7.96 | 7.31  |
|                |             | $\Delta_{34}$ | −1.99 | −4.68  | −1.15 |         |
|                |             | $\Delta_{45}$ | 0.72  |        | 1.43  |         |
|                |             | $\Delta_{56}$ | 0.048 |        |        |         |
| Si             | $\Delta_{12}$ | −15.02     | −16.24 | −15.69 | −9.1  |
|                |             | $\Delta_{23}$ | 7.45  | 12     | 8.46  | 3.65  |
|                |             | $\Delta_{34}$ | 0.89  | 3.4185 | 3.13  |         |
|                |             | $\Delta_{45}$ | −1.01 | −1.14  |        |         |
|                |             | $\Delta_{56}$ | 0.62  |        |        |         |
| Mg$_3$Sb$_2$ (0001) | Mg        | $\Delta_{12}$ | −13.52 | −12.55 | −16.3 | −11.8 |
|                |             | $\Delta_{23}$ | 11.24 | 11.85  | 9.22  | −8.62 |
|                |             | $\Delta_{34}$ | 8.66  | −6.23  | 1.65  |         |
|                |             | $\Delta_{45}$ | 2.00  | −0.65  |        |         |
|                |             | $\Delta_{56}$ | −0.32 |        |        |         |
| Si             | $\Delta_{12}$ | −12.56     | 10.63  | 11.68  | 16.92 |
|                |             | $\Delta_{23}$ | 7.31  | −6.31  | −5.33 | 10.96 |
|                |             | $\Delta_{34}$ | −0.57 | −4.126 | 4.43  |         |
|                |             | $\Delta_{45}$ | −1.23 | −1.86  |        |         |
|                |             | $\Delta_{56}$ | −0.51 |        |        |         |
3.3. Stability of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) Surface

The characteristics of the terminating atoms have a significant influence on the surface energy. Therefore, the surface energy of the Mg-terminated and Si-terminated Mg$_2$Si (111) slabs and that of the Mg-terminated and Sb-terminated Mg$_3$Sb$_2$ (0001) slabs were investigated for further insight into the surface stability of the Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) surfaces. It was significant for the chemical potentials of different elements in the analysis of the phase transition and surface energy. Thus, the chemical potentials had to be considered in the calculation of the surface energy. The surface energy of the Mg$_2$Si (111) plane could be expressed as follows [39,40]:

$$\sigma_{\text{Mg}_2\text{Si}(111)} = \frac{1}{2A}[E_{\text{slab}} - N_{\text{Mg}}\mu_{\text{Mg}} - N_{\text{Si}}\mu_{\text{Si}} + PV - TS]$$

where $E_{\text{slab}}$ is the total energy of a relaxed surface slab, $A$ is the surface area of the surface structure, $\mu_i$ ($i = \text{Mg, Si}$) elucidates the chemical potentials of $i$ atoms, and $N_{\text{Mg}}$ and $N_{\text{Si}}$ are the number of Mg and Si in the Mg$_2$Si (111) slab, respectively. Due to the CASTEP being implemented under 0K and typical pressures, PV and TS could be ignored. In general, the surface slab was in equilibrium with the bulk structure after full relaxation; therefore, the chemical potentials of the Mg$_2$Si (111) plane could be expressed by bulk Mg$_2$Si as follows [41]:

$$\mu^\text{bulk}_{\text{Mg}_2\text{Si}} = 2\mu_{\text{Mg}} + \mu_{\text{Si}}$$

$$\mu^\text{bulk}_{\text{Mg}_3\text{Sb}_2} = 2\mu_{\text{Mg}} + \mu_{\text{Si}} + \Delta H$$

where $\mu^\text{bulk}_{\text{Mg}}$ and $\mu^\text{bulk}_{\text{Si}}$ are the total energy of the Mg and Si atoms in the pure metal Mg and Si, respectively; $\Delta H$ is the formation heat of bulk Mg$_2$Si, which is calculated as follows:

$$\Delta H_{\text{Mg}_2\text{Si}} = \left(E_{\text{total}} - N_{\text{Mg}}E_{\text{Mg}} - N_{\text{Si}}E_{\text{Si}}\right)/\left(N_{\text{Mg}} + N_{\text{Si}}\right)$$

where $E_{\text{total}}$ is the total energy of a Mg$_2$Si unit cell; $N_{\text{Mg}}$ and $N_{\text{Si}}$ are the number of Mg and Si atoms in a Mg$_2$Si unit cell, respectively; and $E_{\text{Mg}}$ and $E_{\text{Si}}$ are the energies per Mg and Si atom, respectively. Considering the structural stability of the surface model, the chemical potentials should be lower and meet the following requirements: $\mu_{\text{Mg}} \leq \mu^\text{bulk}_{\text{Mg}}$ and $\mu_{\text{Si}} \leq \mu^\text{bulk}_{\text{Si}}$. Thus, by combining Equations (2) and (3), we calculated the range of $\Delta\mu_{\text{Mg}} = \mu_{\text{Mg}} - \mu^\text{bulk}_{\text{Mg}}$ and the surface energy as follows:

$$\frac{1}{2}\Delta H \leq \mu_{\text{Mg}} - \mu^\text{bulk}_{\text{Mg}} \leq 0$$
\[ \sigma_{\text{Mg}_2\text{Si}(111)} = \frac{1}{A} \left[ E_{\text{slab}} - N_{\text{Si}}\mu_{\text{bulk}}^{\text{Mg}_2\text{Si}} + \left(2N_{\text{Si}} - N_{\text{Mg}}\right)\mu_{\text{Mg}} \right] \] (7)

The surface energy of the Mg$_3$Sb$_2$ (0001) plane was also calculated by using the same method as that used for the Mg$_2$Si (111) slab. Figure 4 shows the relationship between \( \Delta \mu_{\text{Mg}} \) and the calculated surface energy of both Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) with different terminations. This figure shows that the surface energies of the Mg-terminated and the Si-terminated Mg$_2$Si (111) were 1.425–1.546 J/m$^2$ and 1.306–1.43 J/m$^2$, respectively. Additionally, for the Mg$_3$Sb$_2$ (0001) slab, the formation heat was $-2.135$ eV; furthermore, the surface energies of the Mg-terminated and Sb-terminated Mg$_3$Sb$_2$ (0001) were 0.921–1.234 J/m$^2$ and 1.023–1.479 J/m$^2$, respectively. Moreover, the surface energy of the Mg$_3$Sb$_2$ (0001) slab and the Mg$_2$Si (111) slab have to be higher than that of the $\alpha$-Mg surface (0.58 J/m$^2$) from the viewpoint of reference [42]. These results showed that the surface energy of the Si-terminated Mg$_2$Si (111) surface was smaller than that of the Mg-terminated Mg$_2$Si (111) surface over the entire range, which indicated that the Si-terminated surface trended toward a stable value. Moreover, the surface energy of the Sb-terminated Mg$_3$Sb$_2$ (0001) surface was lower than that of the Mg-terminated Mg$_3$Sb$_2$ (0001) surface under the Sb-rich condition, but the Mg-terminated surface energy was lower under the Mg-rich condition.

![Figure 4. Calculated surface energy of Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) as a function of the magnesium chemical potential.](image)

4. Properties of the Mg$_2$Si/Mg$_3$Sb$_2$ Interface

4.1. Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) Interface Model

On the basis of the results of the convergence tests discussed above, the interface model of Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) was constructed with a superlattice geometry, which combined an 11-layer Mg$_2$Si (111) slab and an 11-layer Mg$_3$Sb$_2$ (0001) slab. As both Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) had two different termination structures and three possible symmetry stacking sequences (OT, MT, and HCP), as shown in Figure 5, there were 12 possible Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) models, where the OT and the MT refer to the position of the bottom atom facing the top and the center of the first layer of another surface model, and the HCP refers to the position of the bottom atom facing the second layer of another surface model. Simultaneously, to reduce the number of interactions among the surface atoms, a vacuum layer of 15 Å was stacked on the substrate of the Mg$_3$Sb$_2$ (0001) surface. To keep the periodic boundary conditions, the coherent interface approximation was performed during the super-cell calculation [43,44].
4.2. Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) Interface Stability

The work of adhesion ($W_{ad}$), as a significant evaluation reference for the interfacial bonding strength, is the reversible work against the separation of interfacial atoms [45]. In general, a higher $W_{ad}$ represents a stronger binding ability of the interface, and the $W_{ad}$ of the Mg$_2$Si/Mg$_3$Sb$_2$ interface can be expressed as follows:

$$W_{ad} = \left( E_{Mg_2Si \ total} + E_{Mg_3Sb_2 \ total} - E_{Mg_2Si/Mg_3Sb_2 \ total} \right) / A$$ (8)

where $E_{Mg_2Si \ total}$ and $E_{Mg_3Sb_2 \ total}$ are the total energy of the Mg$_2$Si slab and the Mg$_3$Sb$_2$ slab after full relaxation, respectively; $E_{Mg_2Si/Mg_3Sb_2 \ total}$ is the total energy of the Mg$_2$Si/Mg$_3$Sb$_2$ interface; and $A$ is the interface area.

In general, the energy of the Mg$_2$Si slab and the Mg$_3$Sb$_2$ slab often remains the same for the one interface structure. Thus, the variation and the fitting curves of the unrelaxed interface energy and the interfacial distance ($d_0$) were calculated first to obtain the optimal $W_{ad}$, as shown in Figure 6. This figure shows that the total energy of 12 optimal interface models and $d_0$ of Mg-(OT, MT, HCP)-Sb, Mg-(OT, MT, HCP)-Mg, Si-(OT, MT, HCP)-Sb, and Si-(OT, MT, HCP)-Mg were obtained preliminarily. Moreover, it can be seen that the HCP interface exhibited a minimum interface energy and minimum interfacial distance compared with the other two stacking sequences (OT and MT). In contrast, the HCP stacking structure had a maximum $W_{ad}$. Considering the computational cost and the acquirement of fully relaxed $W_{ad}$, the calculation was performed without relaxation, and the interatomic interactions on distance were not considered. Therefore, the next step was to determine the revised optimal $W_{ad}$ and $d_0$ with different ‘optimal’ $d_0$ after full relaxation.

**Figure 6.** Total energy of the interfacial supercell as a function of the interface distance for 12 different models: (a) Sb-terminated Mg$_3$Sb$_2$ (0001) models and (b) Mg-terminated Mg$_3$Sb$_2$ (0001) models.
The optimal $W_{ad}$ and $d_0$ results for the relaxed geometries of these 12 interfaces are listed in Table 3. Remarkably, a comparison of the $W_{ad}$ and $d_0$ of an unrelaxed interface with those of a fully relaxed interface revealed that $W_{ad}$ and $d_0$ exhibited a slight increase and decrease, respectively, after the full relaxation of the interface. This might be attributed to the interfacial charge redistribution and atomic displacement that occurred in the interface during the relaxation, resulting in considerable improvements in the bonding strength of the interface. In other words, the initial three stacking sequences of the interfacial structure were non-equilibrium states.

Table 3. The Interfacial distance ($d_0$) and interfacial energy ($\gamma_{int}$) after full relaxation.

| Termination | Stacking | Fully Relaxed |
|-------------|----------|---------------|
| Mg$_2$Si (111) | Mg$_3$Sb$_2$ (0001) | $d_0$/Å | $W_{ad}$/J/m$^2$ |
| Mg-Terminated | Mg-Terminated | OT | 2.6 | 0.56 |
| | | MT | 1.8 | 0.79 |
| | | HCP | 1.3 | 0.86 |
| Mg-Terminated | Sb-Terminated | OT | 2.6 | 0.77 |
| | | MT | 1.4 | 1.06 |
| | | HCP | 1.5 | 1.51 |
| Si-Terminated | Mg-Terminated | OT | 2.4 | 1.24 |
| | | MT | 1.8 | 1.91 |
| | | HCP | 1.6 | 2.05 |
| Si-Terminated | Sb-Terminated | OT | 2.2 | 1.35 |
| | | MT | 1.3 | 1.46 |
| | | HCP | 0.9 | 2.54 |

Table 3 shows that both Mg-terminated and Si-terminated Mg$_2$Si (111) surfaces were likely to combine with the Sb-terminated Mg$_3$Sb$_2$ (0001) surface, mainly because the interfacial bonding strength of the Mg–Mg and Si–Mg bonds was inferior to that of the Mg–Sb and Si–Sb bonds. Meanwhile, the interfacial bonding strength of the Si-terminated Mg$_2$Si (111) surface combined with the Mg-terminated and Sb-terminated Mg$_3$Sb$_2$ (0001) surface was stronger than that of the Mg-terminated Mg$_2$Si (111) surface; this was possibly due to the higher bond strength of the covalent bond between Si and Mg, Sb than that of the metal bond between Mg and Mg, Sb, respectively.

Along with the ideal cohesive energy of the interface, the interfacial energy played a significant role in estimating the interfacial stability. The calculation formula of the interfacial energy of the Mg$_2$Si/Mg$_3$Sb$_2$ interface can be expressed as follows [46,47]:

$$\gamma_{int} = \sigma_{Mg_2Si} + \sigma_{Mg_3Sb_2} - W_{ad}$$ (9)

where $\sigma_{Mg_2Si}$ and $\sigma_{Mg_3Sb_2}$ are the surface energy of the Mg$_2$Si (111) and Mg$_3$Sb$_2$ (0001) slabs, respectively. $W_{ad}$ is the work of adhesion of the Mg$_2$Si/Mg$_3$Sb$_2$ interface.

Figure 7 compares the intercorrelations among the interfacial energies of 12 Mg$_2$Si (111)/Mg$_3$Sb$_2$ (0001) interface models as a function of the Mg chemical potential. Compared with the OT and MT stacking structure, as shown in Figure 7, the interfacial energy of the HCP stacking structure was the lowest among all the terminations. In the whole scope of $\Delta \mu_{Mg}$, the interfacial energies for the Mg–HCP–Mg interface, Mg–HCP–Sb interface, Si–HCP–Mg interface, and Si–HCP–Sb interface were 1.486–1.726 J/m$^2$, 1.215–1.515 J/m$^2$, 0.18–0.42 J/m$^2$, and 0.069–0.369 J/m$^2$, respectively. This indicated a higher stability for the HCP stacking sequence of the Mg$_2$Si/Mg$_3$Sb$_2$ interface. Moreover, the Si-terminated Mg$_2$Si (111) and Sb-terminated Mg$_3$Sb$_2$ (0001) interface with the HCP stacking sequence had the lowest interfacial energy, which further implied that this interface configuration was the preferred equilibrium structure for the Mg$_2$Si/Mg$_3$Sb$_2$ interface. Moreover, the Mg–HCP–Mg had the highest interfacial energy of all the HCP stacking structures, which indicated that it had a smaller interfacial stability than the other three interfaces. Simultaneously, all the results of the interfacial
energy for the 12 models were well consistent with the results of $W_{ad}$. Considering the efficiency and simplicity of the analysis, the next section mainly discusses the Mg–HCP–Mg interface, Mg–HCP–Sb interface, Si–HCP–Mg interface, and Si–HCP–Sb interface, because of the better interfacial stability of the HCP stacking structure.

Figure 7. Interfacial energies of 12 interface systems as a function of the magnesium chemical potential.

4.3. Electronic Structure and Bonding

The charge density differences reflected the bonding characteristics through the electric charge transference, which was a critical analysis method for the interface bonding. Therefore, to gain further insight into the bonding feature of the interface, the charge density differences of the four HCP stacking structures after full relaxation are shown in Figure 8. From Figure 8, the charges were distributed more intensively at the interface because of the interfacial charge redistribution and the localised characteristics of the charge transfer. However, the lost charge of the interior atoms distributed around the atoms regularly and presented a slight distortion because of the atomic interaction. Moreover, although chemical bonds were formed among the interfacial Mg, Si, and Sb atoms, the bond strength was different.

Figure 8. Charge density differences ($e/A^3$) after full relaxation for the (a) Mg-HCP-Mg interface, (b) Mg-HCP-Sb interface, (c) Si-HCP-Mg interface, and (d) Si-HCP-Sb interface.
For the Mg–HCP–Mg interface, as shown in Figure 8a, a lower charge density was distributed between the interfacial Mg atom of the Mg$_2$Si side and the Mg atom of the Mg$_3$Sb$_2$ side; this led to the certain ionic feature on the interface. For the Mg–HCP–Sb interface, as shown in Figure 8b, the stronger bonding strength at the interface was obviously observed, and the charge depletion mainly existed near the interfacial Mg atom of the Mg$_2$Si side and the Sb atom of the Mg$_3$Sb$_2$ side, which indicates that the ionic bonding is formed between the interfacial Mg atom and Sb atom. For the Si–HCP–Mg interface, as shown in Figure 8c, the strong bonding strength at the interface was obviously observed, which implies that covalent and covalent bonding in the Si–HCP–Mg interface may have existed. Figure 8d shows that large charges were accumulated in the Si–HCP–Sb interface and the strongest bonding strength, which proves that the metallic and covalent bonds may have formed at the interface. This resulted in a stronger bonding strength at the interface and explained well why among all the interface models, the Si–HCP–Sb interface had the smallest $d_0$ and the highest $W_{ad}$ values. All of these results were highly consistent with the work of adhesion and the interfacial energy, as mentioned in the previous section.

In order to have a further insight into the electronic structure and the interfacial bonding mechanism of the Mg$_3$Sb$_2$ (0001) and Mg$_2$Si (111) interface, the partial density of states (PDOS) of four different HCP interface structures was investigated, as shown in Figure 9.

In Figure 9a, for the Mg–HCP–Mg interface, the interfacial Mg atoms had an obvious non-localised feature, which indicated that the Mg–HCP–Mg interface had stronger metallic features. However, higher DOS values of the interfacial Mg atom of Mg$_2$Si and Mg$_3$Sb$_2$ at the Fermi level signified the presence of electron hybridisation at the interface, which resulted in a lower bonding strength of the Mg–HCP–Mg interface. A comparison of the PDOS of the interfacial Mg atom, Sb atom, and Si atom in the different layers in Figure 9b revealed that the PDOS curves of the interfacial Mg atom of the Mg$_2$Si side and the Sb atom of the Mg$_3$Sb$_2$ side were obviously different from those of the interior layers. An obvious orbital hybridisation was observed between the interfacial Sb-s and Si-s states in the two obvious peaks at $-7.35$ eV and $-9.10$ eV, respectively, which indicated that the covalent bond was formed at the interface. Simultaneously, the DOS values for the interfacial Mg atom and the Sb atom of Mg$_3$Sb$_2$ increased by varying degrees, and those for the interfacial Mg atom and the Si atom of Mg$_2$Si decreased, which led to the appearance of a metallic feature in the interface bonding. Therefore, metallic bonds and covalent bonds coexisted in the Mg–HCP–Sb interface. In Figure 9c, for the curves of the Sb-p orbitals, the interfacial Sb atom on the Mg$_3$Sb$_2$ side had more occupied states than the interior Sb atoms near the interface, which indicated that the interfacial Sb atom had significant metallic bonding at the Si–HCP–Mg interface. In addition, the covalent bond was formed because of the hybridisation between the interfacial Sb-sp state, Si-s state, and Mg-p state in the range of $-8.17$ to $-6.47$ eV, $-9.76$ to $-8.52$ eV, and $-8.26$ to $-6.52$ eV, respectively. Therefore, mixed covalent and metallic bonds also existed at the Si–HCP–Mg interface. For the Si–HCP–Sb interface, as shown in Figure 9d, a comparison of the PDOS curves of the interfacial Si atom and the Sb atom revealed the strong hybridisation between the interfacial Sb-sp and Si-sp orbits. Moreover, the PDOS curves of the interfacial Si atoms were similar to those of the interfacial Sb atoms from $-12.0$ eV to $-2.1$ eV. All this indicated that the Si–HCP–Sb interface had strong covalent bonding, which elucidated well the stronger covalent bonding resulting in a higher $W_{ad}$.
4.4. Heterogeneous Nucleation Analysis of Mg$_3$Sb$_2$/Mg$_2$Si

According to the above-calculated result, the Si–HCP–Sb interface was the most stable interface to be the heterogeneous nucleus of Mg$_2$Si among all the 12 interface models, because of its smallest interfacial energy and highest work of adhesion. Although the calculated properties of the Mg$_3$Sb$_2$ (0001) and Mg$_2$Si (111) interface, such as adhesion work and interfacial energy, were all obtained at 0K, the calculated results were verified to be accurate and practically acceptable for the solid–solid and solid–liquid interfaces at high temperatures [48]. Therefore, the present calculated results theoretically validated the experimental [23] conclusion at high temperatures for the heterogeneous nucleation of Mg$_3$Sb$_2$ on Mg$_2$Si in Mg–Si alloys.
5. Conclusions

To reveal the mechanism of the Mg$_3$Sb$_2$ heterogeneous nucleation on Mg$_2$Si in Mg–Si alloys, the properties of bulk, interface stability (adhesion energy and interfacial energy), and electronic structure and bonding of Mg$_3$Sb$_2$ (0001)/Mg$_2$Si (111) were calculated by using the first-principles methods. Four types of terminations and three interfacial atom stacking sites were compared to investigate the heterogeneous nucleation efficiency of Mg$_3$Sb$_2$ (0001) on Mg$_2$Si (111). The main conclusions were as follows:

1. For both the Mg$_2$Si (111) slab and the Mg$_3$Sb$_2$ (0001) slab, the 11-layered surface achieved bulk-like characteristics. The Sb-terminated Mg$_3$Sb$_2$ (0001) surface and the Si-terminated Mg$_2$Si (111) surface were more stable than the Mg-terminated surface because of the lower surface energy.

2. Compared with all the stacking sequences, the hollow-stacked interfaces were the most stable interface. Moreover, compared with all the terminated interfaces, the Si–HCP–Sb interface was the most stable interface, because of the fact that $W_{ad}$ and the interface spacing of the Si–HCP–Sb interface, Si–HCP–Mg interface, Mg–HCP–Sb interface, and Mg–HCP–Mg interface were 2.54 J/m$^2$ and 0.9 Å, 2.05 J/m$^2$ and 1.6 Å, 1.51 J/m$^2$ and 1.5 Å, and 0.86 J/m$^2$ and 1.3 Å, respectively.

3. The chemical bonding of the Mg–HCP–Mg interfaces presented stronger metallic bonding, which exhibited the highest interfacial energy. The Mg–HCP–Sb interface and the Si–HCP–Mg interface bonding similarly exhibited a mixture of covalent and metallic bonds. In particular, the Si–HCP–Sb interfaces had an obvious strong covalent feature and the smallest interfacial energy, which showed the largest stability interface among the 12 interface models.

Author Contributions: Funding acquisition, G.Z.; conceived and designed the experiments, H.X.; carried out the experiments and data collection, M.W. and Y.F.; writing—original draft preparation and review, M.W.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Shanxi province grant number 201801D221111.

Acknowledgments: The authors truly thank the Natural Science Foundation of Shanxi province for this research.

Conflicts of Interest: Author M.W., G.Z., H.X. and Y.F. has both received research grants from North university of china. We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, the authors declare that they have no conflict of interest.

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