First-principles calculations were performed to study the alloying stability and electronic structure of the Al-based intermetallic compounds AlCu₃, AlCu₂Zr and AlZr₃. The results show that the lattice parameters obtained after the full relaxation of the crystalline cells are consistent with the experimental data, and these intermetallics have a strong alloying ability and structural stability due to their negative formation energies and their cohesive energies. A further analysis revealed that the single-crystal elastic constants at zero-pressure satisfy the requirements for the mechanical stability of cubic crystals. The calculations on Poisson’s ratio show that AlCu₃ is much more anisotropic than the other two intermetallics. In addition, calculations on the densities of states indicate that the valence bonds of these intermetallics are attributed to the valence electrons of Cu 3d states for AlCu₃, Cu 3d and Zr 4d states for AlCu₂Zr, and Al 3s, Zr 5s and 4d states for AlZr₃, respectively. In particular, the electronic structure of the AlZr₃ shows the strongest hybridization.

Keywords: AlCu₃, AlCu₂Zr, first-principles, electronic structure

1 INTRODUCTION

Intermetallics involving aluminum and transition metals (TMs) are known to have a high resistance to oxidation and corrosion, elevated-temperature strength, relatively low density, and high melting points, which make them desirable candidates for high-temperature structural applications. In particular, zirconium can effectively enhance the mechanical strength of the alloys when copper and zinc elements exist in aluminum and Al-based alloys. Adding Zr to the Al-Mg alloys can effectively remove or reduce hydrogen, grain refinement, pinholes, porosity and hot cracking tendency, and so improve the mechanical properties. Many investigations have focused on the constituent binary systems, such as Al-Cu, Al-Zr, and Cu-Zr; however, there has been a lack of systematic theoretical and experimental investigations for binary and ternary systems, especially for ternary alloy systems.

In recent years, first-principles calculations based on the density-functional theory have become an important tool for the accurate study of the crystalline and electronic structures and mechanical properties of solids. In the present study, we report on a systematic investigation of the structural, elastic and electronic properties of Al-based alloys (AlCu₃, AlZr₃ and AlCu₂Zr) using first-principles calculations, and the results are discussed in comparison with the available experimental data and other theoretical results.

2 COMPUTATIONAL METHOD

All the calculations were performed using the Vienna ab-initio Simulation Package (VASP) based on the density-functional theory (DFT). The exchange and correlation energy was treated within the generalized gradient approximation of Perdew–Wang 91 version (GGA-PW91). The interaction between the valence electrons and the ions was described by using potentials generated with Blöchl’s projector augmented wave (PAW) method. The PAW potential used for Al treats the 3s, 3p states as valence states, and the other electron-ion interaction was described by the 3d, 4s valence states for Cu, 5s, 4d, 5p valence states for Zr. A plane-wave energy cut-off was set at 450 eV for the AlCu₃ and AlCu₂Zr, and at 350 eV for the AlZr₃. Brillouin Zone integrations were performed using the Monkhorst-Pack k-point meshes, e.g., the k-point meshes for AlCu₃, AlCu₂Zr, AlZr₃.
3 RESULTS AND DISCUSSION

3.1 Equilibrium properties

The AlCu3 and AlZr3 alloys have the simple cubic Cu3Au (L12 type, space group Pm-3m) structure. The AlCu2Zr alloy is a partially ordered Cu2MnAl-type fcc structure with the Fm-3m space group. Firstly, these crystal structures were optimized with a relaxation of the internal atoms, allowing the total forces on each ion to be less than 0.01 eV/(10–1 nm). The total energy and density of states (DOS) calculations were performed using the conjugate gradient method, and the coordinates of the internal atoms were allowed to relax until the total forces on each ion were less than 0.01 eV/(10–1 nm). The total internal atoms were allowed to relax until the total forces on each ion were less than 0.01 eV/(10–1 nm). The total energy and density of states (DOS) calculations were performed with the linear tetrahedron method using Blöchl corrections.

In order to avoid wrap-around errors, all the calculations were performed using the "accurate" setting within VASP.

In order to compare the alloying abilities of the present compounds, we calculate the formation energy $\Delta H$, which can be given by:

$$\Delta H = \frac{E_{\text{tot}} - N_A E_{\text{atom}}^A - N_B E_{\text{atom}}^B - N_C E_{\text{atom}}^C}{N_A + N_B + N_C}$$

where $E_{\text{tot}}$ is the total energy of the compound at the equilibrium lattice constant, and $E_{\text{atom}}^A$, $E_{\text{atom}}^B$, $E_{\text{atom}}^C$ are the energies of the isolated atoms A, B and C in the free states. $N_A$, $N_B$ and $N_C$ refer to the numbers of A, B and C atoms in each unit cell. The energies of the isolated Al, Cu and Zr atoms are $-0.276$ eV, $-0.254$ eV and $-2.054$ eV, respectively. The cohesive energies ($E_{\text{coh}}$) per atom of all the crystal or primitive cells are calculated from Eq. (1), and the results of the calculations are listed in Table 2. From the calculated values we find that the cohesive energy of AlZr3 is 2.237 eV and 1.413 eV per atom lower than that of AlCu3 and AlCu2Zr, respectively. Therefore, of the three phases, the AlZr3 phase has the highest structural stability, followed by AlCu2Zr and finally the AlCu3. This means that for the AlZr3, AlCu2Zr, and AlCu3 alloys the structural stability is higher with increasing amounts of Zr in the crystal.

Table 2: Total energy $E_{\text{tot}}$, cohesive energy $E_{\text{coh}}$ and formation energy $\Delta H$ of AlCu3, AlCu2Zr and AlZr3

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{tot}}$/eV per atom</th>
<th>$E_{\text{coh}}$/eV per atom</th>
<th>$\Delta H$/eV per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCu3</td>
<td>$-3.897$</td>
<td>$-3.637$</td>
<td>$-0.277$</td>
</tr>
<tr>
<td>AlCu2Zr</td>
<td>$-5.261$</td>
<td>$-4.551$</td>
<td>$-0.310$</td>
</tr>
<tr>
<td>AlZr3</td>
<td>$-7.574$</td>
<td>$-5.964$</td>
<td>$-1.007$</td>
</tr>
</tbody>
</table>


Table 1: Calculated and experimental lattice parameters $a$ (nm), equilibrium volume $V_0$ (nm$^3$), bulk modulus $B_0$ (GPa) and the pressure derivation of the bulk modulus $B'_0$ for AlCu3, AlCu2Zr, AlZr3

<table>
<thead>
<tr>
<th></th>
<th>AlCu3</th>
<th>AlCu2Zr</th>
<th>AlZr3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$/nm</td>
<td>0.3693</td>
<td>0.3607</td>
<td>0.3692</td>
</tr>
<tr>
<td>$V_0$/nm$^3$</td>
<td>50.358$ \cdot 10^{-3}$</td>
<td>244.805$ \cdot 10^{-3}$</td>
<td>84.110$ \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$B_0$/GPa</td>
<td>131.010</td>
<td>128.600</td>
<td>100.800</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>4.47</td>
<td>4.280</td>
<td>3.48</td>
</tr>
</tbody>
</table>

It is known that the stability of a crystal structure is correlated to its cohesive energy, which is often defined as the work that is needed when the crystal is decomposed into single atoms. Hence, the lower the cohesive energy is, the more stable the crystal structure is. In the present study, the cohesive energies ($E_{\text{coh}}$) of the AlCu3, AlCu2Zr and AlZr3 crystal cells can be calculated by:

$$E_{\text{coh}} = \frac{(E_{\text{tot}} - N_A E_{\text{atom}}^A - N_B E_{\text{atom}}^B - N_C E_{\text{atom}}^C)}{N_A + N_B + N_C}$$

where $E_{\text{atom}}^A$, $E_{\text{atom}}^B$, $E_{\text{atom}}^C$ are the energies per atom of the pure constituents A, B and C in the solid states, respectively. And the other variables are as defined for Eq. (1). If the formation energy is negative, the formation of a compound from its elements is usually an exothermic process. Furthermore, the lower the formation energy is, the stronger the alloying ability is, and the more stable the crystal structure is. The calculated energies of Al, Cu and Zr in their respective crystals are $-3.696$ eV, $-3.728$ eV, $-8.457$ eV. The calculated results of these compounds are also listed in Table 2. It is clear that all...
the $\Delta H$ is negative, which means that the structure of these compounds can exist and be stable. A further comparison and analysis showed that the alloying abilities of AlCu2Zr were much stronger than AlCu3 and AlZr3. It should be noticed that the alloying ability of AlZr3 was higher than that of the AlCu3 alloy.

### 3.2 Elastic properties

The density-functional theory has become a powerful tool for investigating the elastic properties of materials (in the limit of zero temperature and in the absence of zero-point motion). For a given crystal it is possible to calculate the complete set of elastic constants by applying small strains to the equilibrium unit cell and determining the corresponding variations in the total energy. The necessary number of strains is imposed by the theory of small strains to the equilibrium unit cell and determining the corresponding variations in the total energy. The total energy variation between the deformed cell and the initial cell, $\epsilon_{ij}$ is the elastic constant, and $\delta$ is the deformation added to the equilibrium cell. The elastic strain energy is also listed in Table 3. For each kind of lattice deformation, the total energy has been calculated for different strains $\gamma = \pm 0.01 n$ ($n = 0, 2$). By means of a polynomial fit, we extracted three values of the second-order coefficients, corresponding to $3(C_{11} - C_{12})$, $3(C_{11} + 2C_{12})/2$ and $2C_{44}$, respectively, the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ were obtained, and the results are shown in Table 4. From Table 4 we can see that our calculation results agree well with the experimental data or other first-principle calculations. These elastic constants satisfy the requirement of mechanical stability for cubic crystals. This shows that AlCu3, AlCu2Zr and AlZr3 have a stable structure. The average bulk modulus is identical to the single-crystal bulk modulus, i.e., $B = (C_{11} + 2C_{12})/3$. Interestingly, we noted that the bulk modulus calculated from the values of the elastic constants is in good agreement with the one obtained through fitting to the Birch-Murnaghan equation of state ($B_0$), giving a consistent estimate of the compressibility for these compounds.

In order to further validate our results, the elastic moduli, such as the shear modulus $G(GPa)$, Young’s modulus $E(GPa)$, Poission’s ratio $\nu$ and anisotropy constant $A$ for a polycrystalline material were also calculated with the single-crystal elastic constants $C_{ij}$, all of these elastic moduli are shown in Table 4. In the present study we adopted Hershey’s averaging method, which has been known to give the most accurate relation between single-crystal and polycrystalline values for a cubic lattice. According to this method, $G$ is obtained by solving the following equation:

$$G = \frac{8}{3} \left( \frac{C_{11} + 4C_{12}}{2} \right) \left( 1 + \frac{2C_{44}}{C_{11}} \right) \left( 1 - \frac{2C_{44}}{C_{11}} \right) \left( \frac{C_{11} - C_{12}}{2C_{44}} \right)$$

The calculated shear moduli $G$ for AlZr3 are the largest, while the quantities for AlCuZr are less than for AlCu3.

Pugh found that the ratio of the bulk modulus to the shear modulus ($B/G$) of polycrystalline phases can predict the brittle and ductile behavior of the materials. A high and low value of $B/G$ is associated with ductility and brittleness, respectively. The critical value which separates ductility from brittleness is about 1.75. From Table 4 we can see that all the $B/G$ ratios are larger than 1.75. Therefore, AlCu3, AlCu2Zr and AlZr3 have good ductility. In contrast, the biggest $B/G$ ratio for AlCuZr indicates that AlCuZr is of very good ductility in these three Al-based alloys. AlCu3 has an intermediate ductility, while AlZr3 has the worst ductility.

Besides $B/G$, the Young’s modulus $E$ and the Poisson’s ratio $\nu$ are important for technological and engineering applications. The Young’s modulus is used to provide a measure of the stiffness of the solid, i.e., the larger the value of $E$, the stiffer the material. According to Hershey’s averaging method, the Young’s modulus is defined as: $E = 9GB/(3B+G)$. Based on the calculated results, we find that AlZr3 has a Young’s modulus that is 18.806 GPa and 24.663 GPa larger than AlCu3 and AlCu2Zr, respectively. This indicates that the AlZr3 phase has the highest stiffness, followed by AlCu3 and finally AlCu2Zr.
been used to measure the shear stability of the lattice, which usually ranges from –1 to 0.5. The greater the value of the Poisson's ratio $v$, the better the plasticity of the materials. So we can see that AlCu$_3$, AlCu$_2$Zr and AlZr$_3$ have a better plasticity.

The elastic anisotropy of the crystals has an important application in engineering materials since it is highly correlated with the possibility of inducing micro-cracks$^{24,30}$. For cubic symmetric structures$^{31}$, the elastic anisotropy is defined as $A = (2C_{44} + C_{12})/C_{11}$. For a completely isotropic material the value of will be 1, while values smaller or bigger than 1 measuring the degree of elastic anisotropy$^{24}$. Interestingly, we note that the values of $A$ (Table 4) do not deviate far from unity, suggesting that the present cubic-structure alloys also do not deviate far from being isotropic. The calculated results also indicate that AlCu$_3$ is much more anisotropic than the other two alloys.

3.3 Density of states

For a better understanding of the electronic characteristic and structural stability, the total density of states (DOS) for AlCu$_3$, AlCu$_2$Zr and AlZr$_3$ were calculated, as shown in Figure 1, as well as the partial density of states (PDOS) of Al, Cu and Zr atoms in these Al-based intermetallic compounds. Figure 1 has evidence for the metallic character of these considered AlCu$_3$, AlCu$_2$Zr and AlZr$_3$ structures because of the finite DOS at the Fermi level. With regard to the total density of states curve of AlCu$_3$, it is clear from Figure 1a that the whole valence band of AlCu$_3$ is located between –7 eV and 9 eV, which is dominated by Cu 3d states and a small contribution from the 3s and 3p states of Al. The valence band of AlZr$_3$ (Figure 1c) can be divided into three areas. The first area is dominated by the valence electron numbers of Al 3s and Zr 4d states are mostly located between –7 eV and –5 eV, the second by the Zr 5s and 4d states located between –4 eV and –3 eV, and the third by Zr 4d states located between –2.8 eV and 3.0 eV. Both below and above the Fermi level, the hybridization between the Al-p states and Zr-d states is strong. Due to the strong hybridization (or covalent interaction) the entire DOS can be divided into bonding and anti-bonding regions, and that a pseudogap resides in between. The characteristic pseudogap around the Fermi level indicates the presence of the directional covalent bonding. The Fermi level located at a valley in the bonding region implies the system has a pronounced stability. It is

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$B$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>$B/G$</th>
<th>$E$ (GPa)</th>
<th>$v$</th>
<th>$A$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCu$_3$</td>
<td>150.707</td>
<td>120.565</td>
<td>81.880</td>
<td>130.612</td>
<td>43.593</td>
<td>2.996</td>
<td>117.686</td>
<td>0.350</td>
<td>1.887</td>
<td>this study</td>
</tr>
<tr>
<td>AlCu$_2$Zr</td>
<td>157.504</td>
<td>115.305</td>
<td>62.685</td>
<td>129.371</td>
<td>41.237</td>
<td>3.137</td>
<td>111.829</td>
<td>0.356</td>
<td>1.528</td>
<td>this study</td>
</tr>
<tr>
<td>AlZr$_3$</td>
<td>148.653</td>
<td>79.387</td>
<td>70.834</td>
<td>102.476</td>
<td>53.400</td>
<td>1.919</td>
<td>136.492</td>
<td>0.278</td>
<td>1.487</td>
<td>this study</td>
</tr>
</tbody>
</table>

Table 4: Calculated elastic constants (GPa) and elastic modulus (bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), Poisson’s ratio $v$ and anisotropy constant $A$) of AlCu$_3$, AlCu$_2$Zr and AlZr$_3$.
also generally considered that the formation of covalent bonding would enhance the strength of the material in comparison with the pure metallic bonding. According to the covalent approach, the guiding principle is to maximize the bonding. Therefore, for a series of compounds having the same structure, the greater the occupancy in the bonding region the higher the stability. It is indeed seen that the structural stability increases from AlCu$_3$ to AlZr$_3$. For AlCu$_2$Zr (see Figure 1b) it is clear that the main bonding peaks between $-6$ eV and $-2$ eV are predominantly derived from the Cu 3d orbits, while the main bonding peaks between the Fermi level and 3 eV predominantly derived from the Zr 4d orbits. It should be noted that the phase stability of intermetallics depends on the location of the Fermi level and the value of the DOS at the Fermi level, i.e. $N(E_F)$. A lower $N(E_F)$ corresponds to a more stable structure. The value of the total DOS at the Fermi level is 3.64 states per eV for AlZr$_3$, and the value of the total DOS at the Fermi level is 5.74 states per eV for AlCu$_2$Zr. Therefore, AlZr$_3$ has a more stable structure in these three Al-based intermetallics. This is in accordance with the calculation of cohesive energy.

4 CONCLUSIONS

In summary, using the first-principles method we have calculated the alloying stability, the electronic structure, and the mechanical properties of AlCu$_3$, AlCu$_2$Zr and AlZr$_3$. These intermetallics have a strong alloying ability and structural stability due to the negative formation energies and the cohesive energies. In particular, AlCu$_3$ is much more anisotropic than the other two intermetallics. The valence bonds of these intermetallics are attributed to the valence electrons of the Cu 3d states for AlCu$_3$, Cu 3d and Zr 4d states for AlCu$_2$Zr, and Al 3s, Zr 5s and 4d states for AlZr$_3$, respectively, and the electronic structure of the AlZr$_3$ shows the strongest hybridization, leading to the worst ductility.

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