

STRUCTURAL STABILITY AND ELECTRONIC PROPERTIES OF AlCu_3 , AlCu_2Zr AND AlZr_3

STABILNOST STRUKTURE IN ELEKTRONSKE LASTNOSTI AlCu_3 , AlCu_2Zr IN AlZr_3

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First-principles calculations were performed to study the alloying stability and electronic structure of the Al-based intermetallic compounds AlCu_3 , AlCu_2Zr and AlZr_3 . 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 AlCu_3 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 the AlCu_3 , Cu 3d and Zr 4d states for AlCu_2Zr , and Al 3s, Zr 5s and 4d states for AlZr_3 , respectively. In particular, the electronic structure of the AlZr_3 shows the strongest hybridization.

Keywords: AlCu_3 , AlCu_2Zr , first-principles, electronic structure

Narejeni so bili prvi načelni izračuni stabilnosti legiranja in elektronske strukture aluminijevih intermetalnih zlitin (AlCu_3 , AlCu_2Zr in AlZr_3). Rezultati kažejo, da se mrežni parametri po polni relaksaciji kristalnih celic ujemajo z eksperimentalnimi podatki in da imajo te intermetalne zlitine veliko sposobnost legiranja ter stabilno strukturo zaradi negativne tvorbenne energije in kohezivnih energij. Nadaljnje analize so pokazale, da elastična konstanta monokristala pri ničelnem tlaku ustreza zahtevam mehanske stabilnosti kubičnega kristala. Izračun Poissonovega količnika pokaže, da je AlCu_3 bolj anizotropen kot drugi dve intermetalni zlitini. Dodatno izračun gostote stanj pokaže, da so valenčne vezi teh treh intermetalnih zlitin vezane na valenčne elektrone Cu 3d-stanja za AlCu_3 , Cu 3d in Zr 4d-stanja za AlCu_2Zr , ter Al 3s, Zr 5s in 4d-stanja za AlZr_3 , posebno elektronska struktura AlZr_3 pa kaže najmočnejšo hibridizacijo.

Ključne besede: AlCu_3 , AlCu_2Zr , načelen izračun, elektronska struktura

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^{1,2}. In particular, zirconium can effectively enhance the mechanical strength of the alloys when copper and zinc elements exist in aluminum and Al-based alloys³. 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 properties⁴. Many investigations have focused on the constituent binary systems, such as Al-Cu, Al-Zr, and Cu-Zr⁵⁻¹⁰; 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 solids¹¹. In the present study, we report on a systematic investigation

of the structural, elastic and electronic properties of Al-based alloys (AlCu_3 , AlZr_3 and AlCu_2Zr) 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)^{12,13} based on the density-functional theory (DFT)¹⁴. The exchange and correlation energy was treated within the generalized gradient approximation of Perdew-Wang 91 version (GGA-PW91)¹⁵. The interaction between the valence electrons and the ions was described by using potentials generated with Blöchl's projector augmented wave (PAW) method¹⁶. 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 AlCu_3 and AlCu_2Zr , and at 350 eV for the AlZr_3 . Brillouin Zone integrations were performed using the Monkhorst-Pack¹⁷ k-point meshes, e.g., the k-point meshes for AlCu_3 ,

AlCu₂Zr and AlZr₃ were 15×15×15, 9×9×9 and 13×13×13 for optimizing the geometry and calculating the elastic constants, and 25×25×25, 19×19×19 and 23×23×23 for calculations of the density of states (DOS) at the equilibrium volume, respectively. Optimizations of the structural parameters (atomic positions and the lattice constants) for each system 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 energy and density of states (DOS) calculations were performed with the linear tetrahedron method using Blöchl corrections¹⁸. In order to avoid wrap-around errors, all the calculations were performed using the "accurate" setting within VASP.

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^{19,20}. The AlCu₂Zr alloy is a partially ordered Cu₂MnAl-type fcc structure with the Fm-3m space group²¹. Firstly, these crystal structures were optimized with a relaxation of the cell shape and the atomic positions. The equilibrium volume V_0 , bulk modulus B_0 and the pressure derivation of the bulk modulus B'_0 of the AlCu₃, AlCu₂Zr and AlZr₃ were determined by fitting the total energy calculated at different lattice-constant values to a Birch-Murnaghan equation of state²². The results of the first-principles calculations are listed in **Table 1**. From **Table 1** it is clear that the results of our calculations compare very favorably with the experimental data. This shows that the used parameters are reasonable.

It is known that the stability of a crystal structure is correlated to its cohesive energy²³, 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 is²³. In the present study, the cohesive energies (E_{coh}) of the AlCu₃, AlCu₂Zr and AlZr₃ crystal cells can be calculated by:

$$E_{\text{coh}}^{\text{ABC}} = \frac{(E_{\text{tot}} - N_A E_{\text{atom}}^{\text{A}} - N_B E_{\text{atom}}^{\text{B}} - N_C E_{\text{atom}}^{\text{C}})}{N_A + N_B + N_C} \quad (1)$$

Table 1: Calculated and experimental lattice parameters a (nm), equilibrium volume V_0 (nm³), bulk modulus B_0 (GPa) and the pressure derivation of the bulk modulus B'_0 for AlCu₃, AlCu₂Zr, AlZr₃

Tabela 1: Izračunani in eksperimentalno določeni mrežni parametri a (nm), ravnotežni volumen V_0 (nm³), modul pri stiskanju B_0 (GPa) in izpeljava modula iz tlaka B'_0 za AlCu₃, AlCu₂Zr, AlZr₃

	AlCu ₃		AlCu ₂ Zr		AlZr ₃	
	Present.	Expt.	Present.	Expt.	Present.	Expt.
a/nm	0.3693	0.3607 ¹⁹	0.6256	0.6216 ²¹	0.4381	0.4392 ²⁰
V_0/nm^3	$50.358 \cdot 10^{-3}$	–	$244.805 \cdot 10^{-3}$	$240.210 \cdot 10^{-3}$ ²¹	$84.110 \cdot 10^{-3}$	$84.700 \cdot 10^{-3}$ ²⁰
B_0/GPa	131.010	–	128.600	–	100.800	101.4 ⁷
B'_0	4.47	–	4.280	–	3.48	3.33 ⁷

where E_{tot} is the total energy of the compound at the equilibrium lattice constant, and $E_{\text{atom}}^{\text{A}}$, $E_{\text{atom}}^{\text{B}}$, $E_{\text{atom}}^{\text{C}}$ are the energies of the isolated atoms A, B and C in the freedom 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_{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_{tot} , cohesive energy E_{coh} and formation energy ΔH of AlCu₃, AlCu₂Zr and AlZr₃

Tabela 2: Celotna energija E_{tot} , kohezivna energija E_{coh} in tvorbeno energija ΔH za AlCu₃, AlCu₂Zr in AlZr₃

Compound	E_{tot} /eV per atom	E_{coh} /eV per atom	ΔH /eV per atom
AlCu ₃	–3.897	–3.637	–0.177
AlCu ₂ Zr	–5.261	–4.551	–0.359
AlZr ₃	–7.574	–5.964	–0.307

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

$$\Delta H_{\text{ABC}} = \frac{(E_{\text{tot}} - N_A E_{\text{solid}}^{\text{A}} - N_B E_{\text{solid}}^{\text{B}} - N_C E_{\text{solid}}^{\text{C}})}{N_A + N_B + N_C} \quad (2)$$

where $E_{\text{solid}}^{\text{A}}$, $E_{\text{solid}}^{\text{B}}$, $E_{\text{solid}}^{\text{C}}$ 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 is²³. 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 ΔH 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 crystal symmetry²⁴. For a material with cubic symmetry, there are only three independent elastic constants, C_{11} , C_{11} and C_{11} . The strain tensor is given by:

$$\delta = \begin{pmatrix} \delta_{11} & \delta_{12} & \delta_{13} \\ \delta_{21} & \delta_{22} & \delta_{23} \\ \delta_{31} & \delta_{32} & \delta_{33} \end{pmatrix} \quad (3)$$

In the present study we applied three kinds of strains $\delta^{(N)}$ ($N = 1, 2, 3$) so as to obtain the elastic constants, and they are listed in **Table 3**. The first strain is a volume-conserving tetragonal deformation along the z axis, the second refers to a uniform hydrostatic pressure, and the last one corresponds to a volume-conserving orthorhombic shear²⁴. The elastic strain energy was given by:

$$U = \frac{\Delta E}{V_0} = \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \quad (4)$$

where $\Delta E = E_{\text{total}}(V_0, \delta) - E_{\text{total}}(V_0, 0)$ is the total energy variation between the deformed cell and the initial cell, V_0 is the equilibrium volume of the cell, C_{ij} is the elastic constant and δ 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 $\gamma = \pm 0.01n$ ($n = 0 \approx 2$). 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 obtained²⁵, and the results are shown in **Table 4**. From **Table 4** we can see that our calculation results agree

Table 3: The strains used to calculate the elastic constants of AlCu₃, AlCu₂Zr and AlZr₃, with $\gamma = \pm 0.01n$ ($n = 0 \approx 2$)

Table 3: Napetosti, uporabljene za izračun konstant elastičnosti AlCu₃, AlCu₂Zr in AlZr₃, $z \gamma = \pm 0.01n$ ($n = 0 \approx 2$)

Strain	Parameters (unlisted $\delta_{ij} = 0$)	$\Delta E/V_0$ to $0(\gamma^2)$
$\delta^{(1)}$	$\delta_{11} = \delta_{22} = \gamma, \delta_{33} = [(1+\gamma)^2 - 1]$	$3(C_{11} - C_{12})\gamma^2$
$\delta^{(2)}$	$\delta_{11} = \delta_{22} = \delta_{33} = \gamma$	$(3/2)(C_{11} + 2C_{12})\gamma^2$
$\delta^{(3)}$	$\delta_{12} = \delta_{21} = \gamma, \delta_{33} = [\gamma^2(1 - \gamma^2)^{-1}]$	$2C_{44} \gamma^2$

well with the experimental data or other first-principle calculations. These elastic constants satisfy the requirement of mechanical stability for cubic crystals²⁴: $(C_{11} - C_{12}) > 0$, $C_{11} > 0$, $C_{44} > 0$, $(C_{11} + 2C_{12}) > 0$. 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 estimation of the compressibility for these compounds²⁶.

In order to further validate our results, the elastic modulus, such as the shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν 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 method²⁷, which has been known to give the most accurate relation between single-crystal and polycrystalline values for a cubic lattice²⁸. According to this method, G is obtained by solving the following equation:

$$G^3 + \frac{5C_{11} + 4C_{12}}{8} G^2 - \frac{C_{44}(7C_{11} - 4C_{12})}{8} G - \frac{C_{44}(C_{11} - C_{12})(C_{11} + C_{12})}{8} = 0 \quad (5)$$

The calculated shear moduli G for AlZr₃ are the largest, while the quantities for AlCu₂Zr are less than for AlCu₃.

Pugh²⁹ 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 are associated with ductility and brittleness, respectively. The critical value which separates ductility from brittleness is about 1.75. From B/G calculated in **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 AlCu₂Zr indicates that AlCu₂Zr 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 ν 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 material²⁴. According to Hershey's averaging method, the Young's modulus is defined as: $E = 9GB/3(B+G)$. 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 the AlCu₂Zr. In addition, the Poisson's ratio ν has also

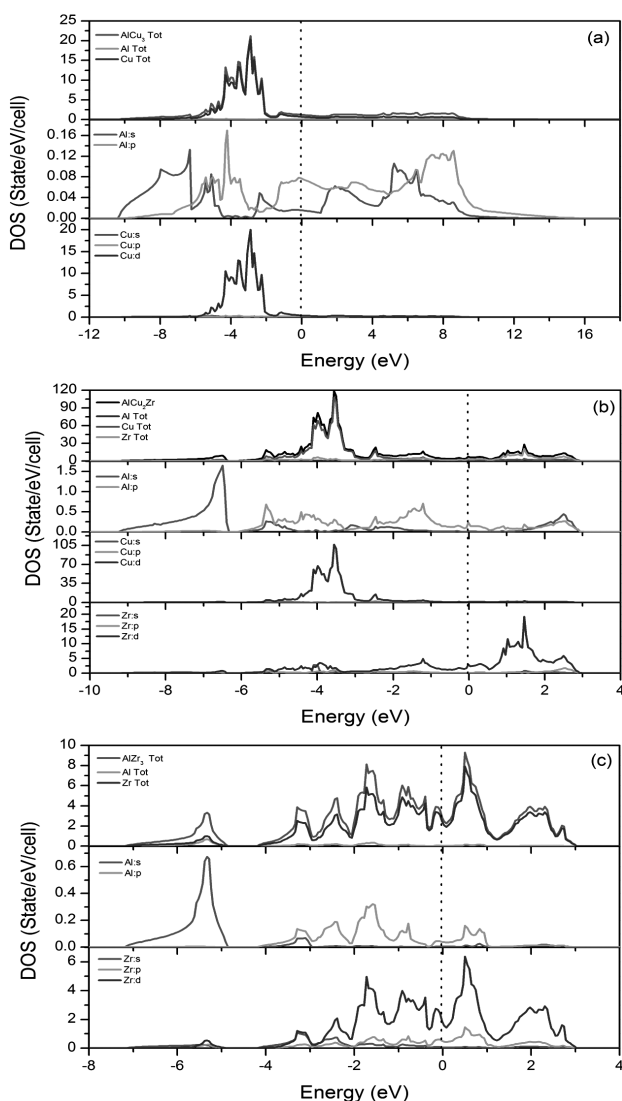
Table 4: Calculated elastic constants (GPa) and elastic modulus (bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and anisotropy constant A) of AlCu_3 , AlCu_2Zr and AlZr_3 **Tabela 4:** Izračunane konstante elastičnosti (GPa) in elastični moduli (modul pri stiskanju B (GPa), strižni moduli G (GPa), Youngovi moduli E (GPa), Poissonov količnik ν in konstante anizotropije A) za AlCu_3 , AlCu_2Zr in AlZr_3

Compound	C_{11}	C_{12}	C_{44}	B	G	B/G	E	ν	A	reference
AlCu_3	150.707	120.565	81.880	130.612	43.593	2.996	117.686	0.350	1.887	this study
	176.000	117.400	92.400	136.900	49.600		132.800	0.340		5
AlCu_2Zr	157.504	115.305	62.685	129.371	41.237	3.137	111.829	0.356	1.528	this study
AlZr_3	148.653	79.387	70.834	102.476	53.400	1.919	136.492	0.278	1.487	this study
	163.800	79.300	86.500	107.670						6

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 ν , the better the plasticity of

the materials. So we can see that AlCu_3 , AlCu_2Zr 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 structures³¹, 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 anisotropy²⁴. 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.

**Figure 1:** The total and partial density of states (DOS) of: a) AlCu_3 crystal cell, b) AlCu_2Zr crystal cell, c) AlZr_3 crystal cell. The vertical dot line indicates the Fermi level.

Slika 1: Skupna in parcialna gostota stanj (DOS) za: a) kristalno celico AlCu_3 , b) kristalno celico AlCu_2Zr , c) kristalno celico AlZr_3 . Navpična pikčasta linija prikazuje Fermijev nivo.

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_2Zr 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_2Zr 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

also generally considered that the formation of covalent bonding would enhance the strength of the material in comparison with the pure metallic bonding³². 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 stability³³. It is indeed seen that the structural stability increases from AlCu_3 to AlZr_3 . For AlCu_2Zr (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. $N(E_F)$ ^{34,35}. 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_2Zr . 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_2Zr 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_2Zr , 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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