Exploration of D0$_{22}$-Type Al$_3$TM(TM = Sc, Ti, V, Zr, Nb, Hf, Ta): Elastic Anisotropy, Electronic Structures, Work Function and Experimental Design

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Abstract: The structural properties, elastic anisotropy, electronic structures and work function of D0$_{22}$-type Al$_3$TM (TM = Sc, Ti, V, Zr, Nb, La, Hf, Ta) are studied using the first-principles calculations. The results indicate that the obtained formation enthalpy and cohesive energy of these compounds are in accordance with the other calculated values. It is found that the Al$_3$Zr is the most thermodynamic stable compound. The mechanical property indexes, such as elastic constants, bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio, and Vickers hardness are systematically explored. Moreover, the calculated universal anisotropic index, percent anisotropy and shear anisotropic factors of D0$_{22}$-type Al$_3$TM are analyzed carefully. It demonstrates that the shear modulus anisotropy of Al$_3$La is the strongest, while that of Al$_3$Ta is the weakest. In particular, the density of states at Fermi level is not zero, suggesting that these phases have metal properties and electrical conductivity. More importantly, the mechanisms of correlation between hardness and Young’s modulus are further explained by the work function. Finally, the experimental design proves that D0$_{22}$-Al$_3$Ta has an excellent strengthening effect.

Keywords: trialuminides; structural properties; mechanical anisotropy; work function; experimental design; orientation relationship

1. Introduction

With the increasing demand of aerospace and automotive industry for structural material properties, aluminum rich compounds containing transition metal (TM, i.e., Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta) elements have attracted extensive attention [1–3]. Among them, trialuminides (Al$_3$TM) are the most potential candidate compounds, mainly because it can meet a variety of advantages, such as a high melting point, good thermal conductivity, low temperature damage resistance, strong creep resistance, and high specific strength. Furthermore, most of these intermetallics have different crystal structures of L1$_2$, D0$_{19}$, D0$_{22}$, or D0$_{23}$ [4–11]. Usually, the Al$_3$TM series of trialuminides can crystallize into the cubic L1$_2$ (space group Pm3m) and tetragonal D0$_{22}$ (space group I4/mmm) crystal structures. The L1$_2$ structure has better ductility due to its higher symmetry and more slip systems. However, it is generally believed that the lower symmetry of D0$_{22}$ structure is the main cause of poor ductility. Many attempts had been made to convert D0$_{22}$ into L1$_2$, which can make the aluminide have good ductility [12–15]. However, the D0$_{22}$ structure has a good strengthening effect in the recent design of high entropy alloy. Hereinto, one of the critical challenges is to explore the internal mechanism of D0$_{22}$-type trialuminides.

Previous studies have made a lot of efforts to reveal the properties of these intermetallic compounds. Recently, Jahnatek M et al. [16] investigated the interatomic bonds and the
tensile anisotropy of Al$_3$(Sc, Ti, V, Cr) by using density-functional theory. Here, in both the L1$_2$ and D0$_{22}$ crystal structure, the main bonding character originates from the saturation of dominant d$^5$ (L1$_2$) and d$^4$ (D0$_{22}$) hybrid orbitals located on the TM atoms. In addition, the structural, electronic, and thermodynamic properties of Al$_3$(Ti, V$_{1-x}$) alloy in D0$_{22}$ and L1$_2$ structures have been reported using the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of the density functional theory (DFT) [17]. It can be drawn from this result that D0$_{22}$ is the relatively stable phase used in these materials, while L1$_2$ is always the metastable phase. In addition, the phase of Al$_3$(Ti, V) crystal and electronic structure in D0$_{22}$ and L1$_2$ were studied in detail, which indicates that the increase of charge density along the Al-(V, Ti) bond is a characteristic of bonding [18,19].

Moreover, Schwarz et al. [20] had explored the properties of trialuminides with ultra-fine microstructures. It can be concluded that the D0$_{22}$ structure has poor ductility because of low symmetry, which may be related to the insufficient number of slip systems in polycrystals. Chen Z et al. [21] had investigated the thermodynamic, elastic, and electronic properties of D0$_{22}$-type Al$_3$V and Al$_3$Nb intermetals under pressures using the first-principle method. Under the same pressure condition, the relative volume change of Al$_3$Nb is smaller than that of Al$_3$V, which is mainly because the bulk modulus of Al$_3$Nb is larger than that of Al$_3$V. By employing the Vienna ab initio simulation package (VASP), the relative stabilities of L1$_2$, D0$_{22}$ and D0$_{23}$ with different structures in the intermetallic compound ZrAl$_3$ were studied by Colinet C et al. [22]. The last theoretical calculations had shown that the structure of D0$_{22}$ is slightly more stable than that of L1$_2$. Li R et al. [23] studied the structural stability, electronic structures, and thermodynamic properties of HfAl$_3$ with L1$_2$, D0$_{22}$ and D0$_{23}$ different structures by the first-principle method. The calculated results revealed that the order of their structural stability can be arranged as D0$_{23}$>D0$_{22}$>L1$_2$. Furthermore, Boulechar R et al. [24] conducted the investigation of the structural stability, electronic, and thermodynamic properties of Al$_3$Ta intermetallic compound by using the full-potential linearized augmented plane wave (FP-LAPW) computational approach. The conclusion is that the total energy and the total density of states at the Fermi level indicate that the stability of D0$_{22}$ structure is better than that of D0$_{23}$ and L1$_2$ structures. Li C et al. [25] calculated the properties of intermetallic compound Al$_3$TM (TM = Ti, Zr, Hf, Sc) and the interfacial properties of Al$_3$TM (TM = Ti, Zr, Hf, Sc) by the first principles. The calculated energy shows that Al$_3$Zr has the lowest formation enthalpies and is the easiest to form.

However, few systematic investigations have been performed regarding the mechanical anisotropy of trialuminides Al$_3$TM (TM, i.e., Sc, Ti, V, Zr, Nb, La, Hf, Ta). Particularly, up to now, the first-principles study of work function of these trialuminides Al$_3$TM phases is almost blank. Accordingly, it is interesting to research the differences and similarities in elastic properties when the Al element forms a bond with those transition elements. Therefore, further attempts in this respect still need to research the properties of D0$_{22}$-type trialuminides.

Indeed, when the properties of compounds are to be explored and cannot be measured by experimental means, theoretical simulation is a very effective method to forecast the properties of materials. Faithfully, the first principles calculation method based on the density functional theory (DFT) is a very powerful way to accurately study the physical properties of compounds [26,27]. Consequently, the structure, mechanical anisotropy, electronic properties, and work function of trialuminides Al$_3$TM (TM, i.e., Sc, Ti, V, Zr, Nb, La, Hf, Ta) have been systematically explored by first-principles calculation method in the present work. Based on the simulation results, an experiment was designed to verify the simulation results. The research results can supply more theoretical and technological guidance on D0$_{22}$-type trialuminides design.

2. Methods and Details

In order to more systematically study the internal mechanisms of D0$_{22}$ structure Al$_3$TM (TM = Sc, Ti, V, Zr, Nb, La, Hf, Ta), the first-principle calculations based on
density functional theory are implemented in the CASTEP (Cambridge Serial Total Energy Package) code [28]. The generalized gradient approximation (GGA) method is applied to the exchange correlation function, and three parameterization ways, Perdew, Burke, and Ernzerhof (PBE) are adopted [29,30]. The 3s²3p¹, 3s²3d¹4s², 3s²3p⁶3d²4s², 3s²3p⁶3d³4s², 4d¹5s³, 4s⁴p⁶4d²5s², 4s⁴p⁶4d⁴5s¹, 5s²5p⁶5d¹6s², 5d²6s² and 5d⁵6s² electrons are explicitly considered as valence for Al, Sc, Ti, V, Zr, Nb, La, Hf and Ta, respectively. In the process of optimization, the total energy of the self-consistent convergence condition is less than 1.0 × 10⁻⁵ eV/atom. The maximum displacement is 0.001 Å and the maximum force acting on each atom is 0.03 eV/Å. The maximum stress deviation is 0.05 GPa, while the SCF convergence accuracy is set to 5.0 × 10⁻⁷ eV/atom. Using plane wave basis set, the cutoff energy is 500 eV, while the total energy of this work will eventually converge to less than 1 meV. Based on the characteristics of D0₂₂ crystal type in this study, the k-point grid of energy integration in irreducible Brillouin region is generated by using the Monkhorst-Pack method. A 22 × 22 × 10 k-point mesh for the static calculation is used for this work.

Based on the simulation results, we designed an experiment to verify the simulation results. A high entropy alloy reinforced by D0₂₂-type Al₃Ta phase was designed. Several elements of Co, Cr, Fe, Ni and Ta powders with purity of 99.96% were used as designed materials (Co 21.6 ± 0.2, Cr 19.8 ± 0.3 Fe 21.5 ± 0.2 Al 35.5 ± 0.3 Ta 1.6 ± 0.2 with atomic percentage). These nearly pure powders were first ball-ground and then pressed into shape. Finally, it is sintered in a vacuum tube furnace. To ensure uniformity, the alloy is smelted five times and then soldered at 1200 °C. At last, the X-ray diffraction (XRD) was tested at room temperature and operated at 30 kV, 50 mA, with Cu Kα radiation. The instrument model was D/Max-2550 X-ray diffractometer (Rigaku Inc, Tokyo, Japan). The data of XRD were analyzed with JADE software (version 6.5, Jade, Christchurch, New Zealand). At the same time, the samples were characterized by scanning electron microscope (SEM SU6600, Hitachi High-Technology Corp., Tokyo, Japan) and transmission electron microscope (TEM JEOL 2100 F, JEOL Co., Ltd., Tokyo, Japan).

3. Results and Discussion
3.1. Structural Properties and Stability

Firstly, the structural stability of these D0₂₂-type compounds was investigated. The crystal structure of the binary compound D0₂₂-Al₃TM, where TM is Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta, is displayed in Figure 1. The D0₂₂-type compounds are tetragonal crystal with a space group of I4/mmm. Except for Al element, the composition of these compound elements is mainly composed of transition elements. Although these transition elements form the same crystal structure with aluminum, they have a greater impact on the properties of the compound. Being able to understand their internal mechanisms is very important for the design of alloys.

Figure 1. The crystal structure of D0₂₂-type Al₃TM compounds.
In order to determine the phase stability of Al₃TM (TM = Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta) intermetallics, the formation enthalpy and cohesive energy of these compounds are calculated by following equations [31,32]:

\[
\Delta H = \frac{1}{x + y} \left( E_{\text{tot}} - xE_{\text{solid}}^A - yE_{\text{solid}}^B \right),
\]

(1)

\[
E_{\text{coh}} = \frac{1}{x + y} \left( E_{\text{tot}} - xE_{\text{atom}}^A - yE_{\text{atom}}^B \right),
\]

(2)

where \( \Delta H \) is the formation enthalpy of Al₃TM compound. \( E_{\text{tot}} \) is the total energy of Al₃TM phase. \( E_{\text{solid}}^A \) and \( E_{\text{solid}}^B \) are the energy of Al and TM atom, respectively. In addition, \( E_{\text{coh}} \) is the cohesive energy of Al₃TM compound. \( E_{\text{atom}}^A \) and \( E_{\text{atom}}^B \) is the energy of Al and TM free atom, respectively. The \( x \) and \( y \) are the number of Al and TM atom in the D0₂₂-Al₃TM crystal structure, respectively. The calculated results of this work are noted in Table 1 and compared with other previous values [13,21,32,33]. The order of the compounds is arranged according to the atomic number of the TM atom in the periodic table of the elements. After analysis, it is evidence that the obtained results are basically coincident with the other calculated values, which indicates the reliability and good self-consistency of the proposed method.

### Table 1. The calculated lattice constant (\( a, c \) in Å), density (\( \rho \), g/cm³), volume (\( V \), Å³), \( \Delta H \) (eV/atom) and \( E_{\text{coh}} \) (eV/atom) of the Al₃TM compounds.

| Species | Atomic Number | a  | c  | \( \rho \) | \( V \) | \( \Delta H \) | \( E_{\text{coh}} \) |
|---------|---------------|----|----|----------|--------|-----------|---------------|
| Al₃Sc   | 21            | 4.024 | 8.840 | 2.920 | 143.173 | -0.366 | -4.221 |
| Al₃Ti   | 22            | 3.950 | 8.630 | 3.346 | 127.892 | -0.396 | -4.793 |
| Al₃V    | 23            | 3.773 | 8.324 | 3.697 | 118.484 | -0.283 | -4.846 |
| Al₃Y    | 39            | 4.194 | 9.260 | 3.464 | 162.863 | -0.295 | -4.178 |
| Al₃Zr   | 40            | 3.963 | 9.027 | 4.034 | 141.757 | -0.464 | -4.916 |
| Al₃Nb   | 41            | 3.854 | 8.641 | 4.497 | 128.382 | -0.419 | -5.473 |
| Al₃La   | 57            | 4.454 | 9.240 | 3.984 | 183.279 | -0.134 | -3.934 |
| Al₃Hf   | 72            | 3.946 | 9.918 | 6.206 | 138.842 | -0.406 | -4.906 |
| Al₃Ta   | 73            | 3.857 | 8.598 | 6.789 | 128.121 | -0.322 | -5.151 |

The first principle calculation is carried out at the ground state of 0 K and 0 Pa. The formation enthalpy of the compound is negative, indicating that the formation of the compound is an exothermic process. The more negative the formation enthalpy, the more stable the compound is. It can be seen from Table 1 that the formation enthalpy of these nine D0₂₂-type compounds is less than zero, meaning that these compounds are thermodynamically stable in the ground state.

It is clear from Table 1 that the calculated value of cohesive energy of these compounds is \(-4.221, -4.793, -4.846, -4.178, -4.916, -5.473, -3.934, -4.906, -5.151\) eV/atom for Al₃Sc, Al₃Ti, Al₃V, Al₃Y, Al₃Zr, Al₃Nb, Al₃La, Al₃Hf, Al₃Ta, respectively. Generally speaking, the large cohesive energy of compounds can only show that the free atoms of the two elements release more energy when they bond. If the energy needed to break the combination of the two elements is also large, the compound is still relatively unstable. However, the thermodynamic stability of compounds is affected by their enthalpy of formation. To some extent, the lower the enthalpy of formation, the easier the compounds are to form and the higher the thermodynamic stability [35,36]. The results show that the value of formation enthalpy of these D0₂₂-type compounds is \(-0.366, -0.396, -0.283, -0.295, -0.464, -0.419, -0.134, -0.406, -0.322\) eV/atom for Al₃Sc, Al₃Ti, Al₃V, Al₃Y.
Al$_3$Zr, Al$_3$Nb, Al$_3$La, Al$_3$Hf, Al$_3$Ta, respectively. The formation enthalpy of Al$_3$Zr is the lowest, which suggests that Al$_3$Zr alloy has the strongest formation ability and the most stable thermodynamics, while Al$_3$La is on the contrary. Therefore, the alloying ability of the nine D0$_{22}$-type compounds from strong to weak can be arranged as Al$_3$Zr > Al$_3$Nb > Al$_3$Hf > Al$_3$Ti > Al$_3$Sc > Al$_3$Ta > Al$_3$Y > Al$_3$V > Al$_3$La, as showed in Figure 2. Considering all these compounds together, it is found that the Al$_3$Zr is the most thermodynamic stable compound.

![Figure 2](image_url)

**Figure 2.** The calculated formation enthalpies of Al$_3$TM compounds.

### 3.2. Mechanical Stability, Elastic Properties and Moduli

As well known, elastic constant is a very significant index to characterize the properties of compounds. The elastic constant is the index of material elasticity, which is related to the stress-strain relationship in the anisotropic medium. To some extent, the elastic constant also indicates the influence of crystal dynamics on mechanical behavior. The stress-strain method is used to calculate the elastic constants in the present calculation process and the results can be listed in Table 2. Furthermore, for the D0$_{22}$-type crystal, tetragonal phase (C$_{11}$, C$_{33}$, C$_{44}$, C$_{66}$, C$_{12}$, and C$_{13}$) [37], the elastic constants can be restricted by the following Formula (3):

\[
\begin{align*}
C_{11} & > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0 \\
(C_{11} - C_{12}) & > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0, \\
2(C_{11} + C_{12}) + C_{33} + 4C_{13} & > 0.
\end{align*}
\]

(3)

It is noticeable that the elastic constants calculated in Table 2 conform to the mechanical stability criterion. According to Equation (3), these D0$_{22}$-type compounds are mechanically stable at 0 K. The elastic constants C$_{11}$, C$_{22}$, and C$_{33}$ mean the compressibility of the crystal structure along the a-axis, b-axis, and c-axis, respectively. In the tetragonal system, C$_{11}$ and C$_{22}$ have the same value. Similarly, the value of C$_{44}$ in the tetragonal system is the same as that of C$_{55}$. The value of C$_{44}$ indicates the ability to resist shear strain in (100) or (010) plane, while the value of C$_{66}$ represents the ability to resist shear strain in (001) plane. In view of Al$_3$Sc, Al$_3$Y and Al$_3$La compounds, the calculated value of C$_{33}$ is less than that of C$_{11}$, which proves that the a-axis has greater compression resistance than the c-axis. However, for other compounds, such as Al$_3$Ti, Al$_3$V, Al$_3$Zr, Al$_3$Nb, Al$_3$Hf, Al$_3$Ta, the elastic constants of C$_{33}$ are higher than that of C$_{11}$, suggesting that the c-axis has greater compression resistance than the a-axis, as illustrated in Figure 3. In particular, it was found that Al$_3$Ta has the highest resistance along the a-axis, b-axis, and c-axis. Besides, the values of C$_{11}$ and C$_{33}$ are larger than that of C$_{44}$ and C$_{66}$. It means that these D0$_{22}$-type phases are highly deformation resistant under uniaxial stress along the a- and c-axis.
Table 2. The calculated elastic constants $C_{ij}$ (GPa) of $\text{Al}_3\text{TM}$ compounds.

| Species | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ |
|---------|---------|---------|---------|---------|---------|---------|
| $\text{Al}_3\text{Sc}$ | 156.86 | 56.88 | 42.17 | 145.14 | 67.20 | 95.17 |
| $\text{Al}_3\text{Ti}$ | 158.00 [13] | 60.00 [13] | 42.00 [13] | 158.00 [13] | 63.00 [13] | 93.00 [13] |
| $\text{Al}_3\text{V}$ | 192.06 | 84.53 | 44.60 | 215.66 | 94.46 | 126.42 |
| $\text{Al}_3\text{Zr}$ | 192.00 [13] | 84.00 [13] | 49.00 [13] | 216.00 [13] | 94.00 [13] | 122.00 [13] |
| $\text{Al}_3\text{Y}$ | 227.01 | 89.03 | 45.95 | 258.69 | 99.37 | 130.55 |
| $\text{Al}_3\text{Sc}$ | 233.00 [13] | 77.00 [13] | 47.00 [13] | 258.00 [13] | 104.00 [13] | 129.00 [13] |
| $\text{Al}_3\text{Zr}$ | 220.87 [21] | 92.69 [21] | 45.26 [21] | 256.95 [21] | 98.57 [21] | 130.25 [21] |
| $\text{Al}_3\text{V}$ | 132.51 | 58.63 | 38.77 | 128.45 | 51.60 | 84.84 |
| $\text{Al}_3\text{Ti}$ | 185.96 | 85.34 | 43.13 | 202.08 | 90.00 | 125.22 |
| $\text{Al}_3\text{Nb}$ | 244.54 | 92.28 | 45.94 | 268.13 | 104.57 | 134.22 |
| $\text{Al}_3\text{La}$ | 242.57 [21] | 92.85 [21] | 45.78 [21] | 266.84 [21] | 102.41 [21] | 134.03 [21] |
| $\text{Al}_3\text{Hf}$ | 193.60 [33] | 87.10 [33] | 47.40 [33] | 217.80 [33] | 92.40 [33] | 123.30 [33] |
| $\text{Al}_3\text{Ta}$ | 249.05 | 88.99 | 52.89 | 274.55 | 104.96 | 130.05 |

Figure 3. The trend of elastic constants of $\text{Al}_3\text{TM}$ compounds.

On the other hand, the bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$) and Poisson’s ratio ($\sigma$) of $\text{Al}_3\text{TM}$ crystal can be calculated by Voigt-Reuss-Hill (VRH) approximation method. Using the following formulas [38], the calculated values are shown in Table 3.

$$B_{H} = \frac{1}{2} (B_{V} + B_{R}),$$  \hspace{1cm} (4)

$$G_{H} = \frac{1}{2} (G_{V} + G_{R}),$$  \hspace{1cm} (5)

$$E = \frac{9B_{H}G_{H}}{3B_{H} + G_{H}},$$  \hspace{1cm} (6)

$$\sigma = \frac{(3B_{H} - 2G_{H})}{2(3B_{H} + G_{H})},$$  \hspace{1cm} (7)

where the subscript symbols H denotes the modulus values obtained by the Hill approximation. The subscript V and R mean the modulus values obtained by the Voigt and Reuss approximation methods, respectively. Furthermore, the Voigt approximation limits the maximum of elastic modulus and the Reuss approximation is considered to be the
minimum of elastic modulus. The Hill approximation uses the average value of Voigt and Reuss to express the elastic constants of materials.

Table 3. The calculated bulk modulus (GPa), shear modulus (GPa), Young’s modulus (GPa), B/G, Poisson’s ratio and Vickers hardness (GPa) of Al3TM compounds.

| Species | B_V | B_R | B | G_V | G_R | G | E | σ | B/G | Hv |
|---------|-----|-----|---|-----|-----|---|---|---|-----|----|
| Al3Sc  | 82.37 | 81.91 | 82.14 | 67.09 | 63.88 | 65.49 | 155.21 | 0.185 | 1.25 | 14.72 |
| 92.1 [25] | 91.8 [25] | 91.9 [25] | 74.1 [25] | 71.7 [25] | 72.9 [25] | 173.1 [25] | 0.19 [25] | 1.26 [25] |
| Al3Ti  | 105.25 | 105.14 | 105.19 | 91.47 | 84.71 | 88.09 | 206.60 | 0.173 | 1.19 | 19.32 |
| 107.00 [13] |
| 102.4 [25] | 102.2 [25] | 102.3 [25] | 81.8 [25] | 81.7 [25] | 81.8 [25] | 193.8 [25] | 0.18 [25] | 1.25 [25] |
| Al3V  | 119.40 | 119.35 | 119.37 | 101.31 | 97.05 | 99.18 | 233.01 | 0.175 | 1.20 | 20.70 |
| 118.00 [13] | 118.32 [21] |
| Al3Zr  | 101.91 | 101.61 | 101.76 | 87.87 | 80.58 | 84.23 | 198.04 | 0.176 | 1.21 | 18.45 |
| 100.8 [25] | 100.6 [25] | 100.7 [25] | 84.6 [25] | 83.3 [25] | 84.0 [25] | 197.2 [25] | 0.17 [25] | 1.20 [25] |
| Al3Nb  | 125.06 | 124.89 | 124.98 | 106.88 | 103.25 | 105.06 | 246.20 | 0.172 | 1.19 | 21.85 |
| 124.45 [21] |
| 103.71 [21] | 243.50 [21] | 0.174 [21] | 1.20 [21] |
| Al3La  | 60.09 | 56.78 | 58.43 | 25.94 | 18.88 | 22.41 | 59.62 | 0.330 | 2.61 | 1.02 |
| 106.5 [25] | 106.0 [25] | 106.3 [25] | 77.8 [25] | 77.4 [25] | 77.6 [25] | 187.2 [25] | 0.21 [25] | 1.37 [25] |
| 107.60 [33] |
| 86.60 [33] | 204.80 [33] | 0.180 [33] | 1.24 [33] |
| Al3Ta  | 130.22 | 130.18 | 130.21 | 109.53 | 106.85 | 108.19 | 254.17 | 0.175 | 1.20 | 21.94 |

It is noted that the calculated values of elastic moduli are summarized in the Table 3. Obviously, the bulk modulus of these D022-type compounds decreased in order: Al3Ta > Al3Nb > Al3V > Al3Hf > Al3Ti > Al3Zr > Al3Sc > Al3Y > Al3La, as shown in Figure 4. The bulk modulus of crystal reflects the resistance of crystal under water pressure. At the microscopic level, the bulk modulus of the crystal is determined by the strength of the chemical bond. The larger the bulk modulus of the crystal, the stronger the chemical bond strength and the stronger the compression resistance. The calculated results show that Al3Ta has the strongest resistance of compression. Oppositely, Al3La has the weakest resistance of compression.

![Figure 4. Comparison of moduli and Vickers hardness of different compounds.](image)

Generally, shear modulus refers to the ability of a material to resist shear strain. The higher the shear modulus, the stronger the rigidity of the material. As listed in Table 3,
Al$_3$Ta and Al$_3$La have the largest shear modulus (108.19 GPa) and smallest one (22.41 GPa), respectively. At the same time, Young's modulus is a term of material mechanics, which is used to express the deformation resistance of solid materials. The rigidity of the material can be reflected by the value of Young's modulus. That is to say, the greater the Young's modulus is, the greater the rigidity of the material is, and the harder it is to deform. It can be seen that Al$_3$Ta and Al$_3$La have the largest Young's modulus (254.17 GPa) and smallest one (59.62 GPa). It is evident that Al$_3$Ta has the greater rigidity and is difficult to deform.

Furthermore, the brittleness and ductility of the materials can be judged by Poisson's ratio. This is due to Poisson's ratio being the ratio of transverse strain to longitudinal strain when the material is deformed under tension or compression. A value of 0.26 is taken as the critical value of brittle and plastic separation. When the value of Poisson's ratio is greater than 0.26, it can be considered as ductile material. On the contrary, it can be determined as brittle material. When the value of Poisson's ratio is less than 0.26, it can be judged as brittle material. Otherwise, it can be judged as ductile material [39,40]. As for these D0$_{22}$-type compounds, the Poisson’s ratios are 0.185, 0.173, 0.175, 0.211, 0.176, 0.172, 0.183, and 0.175 for Al$_3$Sc, Al$_3$Ti, Al$_3$V, Al$_3$Y, Al$_3$Zr, Al$_3$Nb, Al$_3$Hf, and Al$_3$Ta respectively, while the Poisson’s ratio of Al$_3$La is 0.330. Therefore, it is noted that Al$_3$La shows toughness and the other eight compounds exhibit brittle property. Similarly, brittleness and ductility of compounds can be predicted by the ratio of bulk modulus to shear modulus [41,42]. Based on the Pugh standard, the material presents brittleness when the value of B/G is less than 1.75, otherwise the material exhibit toughness. As can be shown in Table 3 that the B/G of Al$_3$Sc, Al$_3$Ti, Al$_3$V, Al$_3$Y, Al$_3$Zr, Al$_3$Nb, Al$_3$Hf, and Al$_3$Ta is less than 1.75, indicating that these eight D0$_{22}$-type compounds are brittle. On the contrary, the B/G value of Al$_3$La is greater than 1.75, which shows toughness.

Ultimately, it is reported that the hardness of a compound is directly related to its shear modulus and Young’s modulus. At present, although the accurate relationship between hardness and elastic modulus has not been determined, the larger elastic modulus can represent the higher hardness. For the nine compounds studied, their Vickers hardness (HV) of Al$_3$TM-type compounds can be forecasted by the following empirical formula [43]:

$$HV = 2\left(\frac{G^3}{B^2}\right)^{0.585} - 3,$$

(8)

As presented in Table 3, the maximum Vickers hardness of Al$_3$TM is Al$_3$Ta, which is 21.94 GPa. The minimum Vickers hardness is Al$_3$La and its value is 1.02 GPa. Similar trends indicate that Al$_3$Ta and Al$_3$La have the largest Young’s modulus and smallest one, as indicated in Figure 4. It is also confirmed that Young’s modulus has a decisive effect on the hardness of the compound.

3.3. Mechanical Anisotropy

It is very important to study the anisotropy of D0$_{22}$-type compounds since this index has influence on the macroscopic mechanical properties of the alloy. In the present calculation, the universal anisotropic index (AU), the percent anisotropy index (AB and AC) and the shear anisotropic factors (A1, A2 and A3) are estimated by the following expressions [44]:

$$AU = 5\left(\frac{G_V}{G_R}\right) + \frac{B_V}{B_R} - 6 \geq 0,$$

(9)

$$AB = \frac{B_V - B_R}{B_V + B_R} \times 100\%,$$

(10)

$$AC = \frac{G_V - G_R}{G_V + G_R} \times 100\%,$$

(11)

$$A_1 = \frac{4C_{14}}{C_{11} + C_{33} - 2C_{13}} \text{ for (100) plane},$$

(12)
The relationship between bulk modulus, shear modulus, Young’s modulus, and different types of D0_{22} can be realized by the following formulas [45,46]:

\[ A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \text{ for } (010) \text{ plane,} \]

\[ A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \text{ for } (001) \text{ plane.} \]

The generated universal anisotropic index ($A^U$), percent anisotropy ($A_B$ and $A_C$) and shear anisotropic factors ($A_1$, $A_2$ and $A_3$) of these D0_{22}-type compounds are exhibited in Table 4. The anisotropy of D0_{22}-type compounds can be directly reflected by the value of $A^U$. In case of $A^U$ is equal to zero, the crystal is isotropic. The larger the value of $A^U$, the stronger the anisotropy, and vice versa. It is noted that the values of $A^U$ of Al$_3$Sc, Al$_3$Ti, Al$_3$V, Al$_3$Y, Al$_3$Zr, Al$_3$Nb, Al$_3$La, Al$_3$Hf, Al$_3$Ta are 0.257, 0.400, 0.220, 0.385, 0.455, 0.177, 1.927, 0.440, and 0.126, respectively. In this case, the anisotropic properties of these D0$_{22}$-type compounds can be listed as Al$_3$La > Al$_3$Zr > Al$_3$Hf > Al$_3$Ti > Al$_3$Y > Al$_3$Sc > Al$_3$V > Al$_3$Nb > Al$_3$Ta.

Table 4. The calculated universal anisotropic index ($A^U$), percent anisotropy ($A_B$ and $A_C$) and shear anisotropic factors ($A_1$, $A_2$ and $A_3$) of Al$_3$TM compounds.

| Species  | $A^U$ | $A_B$ | $A_C$ | $A_1$ | $A_2$ | $A_3$ |
|----------|-------|-------|-------|-------|-------|-------|
| Al$_3$Sc | 0.257 | 0.282 | 2.448 | 1.235 | 1.235 | 1.904 |
| Al$_3$Ti | 0.400 | 0.053 | 3.838 | 1.186 | 1.186 | 2.351 |
| Al$_3$V  | 0.220 | 0.019 | 2.149 | 1.009 | 1.009 | 1.892 |
| Al$_3$Y  | 0.385 | 0.294 | 3.648 | 1.125 | 1.125 | 2.297 |
| Al$_3$Zr | 0.455 | 0.148 | 4.328 | 1.193 | 1.193 | 2.489 |
| Al$_3$Nb | 0.177 | 0.067 | 1.727 | 0.994 | 0.994 | 1.763 |
| Al$_3$La | 1.927 | 2.839 | 15.745 | 0.549 | 0.549 | 2.603 |
| Al$_3$Hf | 0.440 | 0.043 | 4.203 | 1.185 | 1.185 | 2.457 |
| Al$_3$Ta | 0.126 | 0.015 | 1.238 | 1.005 | 1.005 | 1.625 |

When the values of $A_B$ and $A_C$ are not equal to zero, it shows that the bulk modulus and shear modulus of the crystal are anisotropic. The values of $A_B$ and $A_C$ correspond to the anisotropy. It reveals that Al$_3$La has the largest $A_B$ value 2.839, indicating that the bulk modulus anisotropy of Al$_3$La is the strongest. Then, the bulk modulus anisotropy of Al$_3$Y, Al$_3$Sc, Al$_3$Zr, Al$_3$Nb, Al$_3$Ti, Al$_3$Hf, Al$_3$V, and Al$_3$Ta decrease gradually. Evidently, the $A_C$ value of Al$_3$La is the highest and that of Al$_3$Ta is the lowest, indicating that Al$_3$La and Al$_3$Ta have the strongest and weakest shear modulus anisotropy, respectively.

Furthermore, the shear factors $A_1$, $A_2$, and $A_3$ can be used to represent anisotropy on (100), (010), and (001) planes. When the values of $A_1$, $A_2$, and $A_3$ are 1, the crystal is isotropic. According to the calculated results, all D0$_{22}$-type compounds have different degrees of elastic anisotropy, as noted in the Table 4. Among these D0$_{22}$-type phases, the $A_1$ ($A_2$) values of Al$_3$La deviate most severely from 1, which imply that Al$_3$La exhibits the strongest shear anisotropy in (100) and (010) planes. Conversely, the values of $A_1$ ($A_2$) of Al$_3$Ta have the least deviation among these D0$_{22}$-type compounds, which mean that the Al$_3$Ta exists the lowest shear anisotropy in the (100) plane and (010) plane. The $A_2$ value of Al$_3$La has the most deviation from 1, hinting that the Al$_3$La shows the highest shear anisotropy in the (001) plane. These D0$_{22}$-type phases all have a wide deviation from 1 in the (001) plane.

On the other hand, the three-dimensional (3D) image has the characteristics of clear hierarchy and visual intuition, which can show the anisotropic characteristics of these D0$_{22}$-type compounds more clearly and vividly. In this study, bulk modulus, shear modulus, and Young’s modulus of different D0$_{22}$-type compounds are drawn with spherical coordinates. The relationship between bulk modulus, shear modulus, Young’s modulus, and different directions can be realized by the following formulas [45,46]:

\[ \frac{1}{B} = (S_{11} + S_{12} + S_{13}) (l_1^2 + l_2^2) + (2S_{13} + S_{33})l_3^2. \]
\[
\frac{1}{G} = \frac{1}{2} (S_{66} + S_{44}) + (4S_{11} - 4S_{12} - 2S_{66})l_1^2l_2^2 + (2S_{11} + 2S_{33} - 4S_{13} - 2S_{44}) \left( l_1^2l_3^2 + l_2^2l_3^2 \right) + \frac{1}{2} (S_{44} - S_{66})l_3^2,
\]

(16)

\[
\frac{1}{E} = S_{11} \left( l_1^4 + l_2^4 \right) + (2S_{13} + S_{44}) \left( l_1^2l_2^2 + l_2^2l_3^2 \right) + S_{33}l_3^4 + (2S_{12} + S_{66})l_1^2l_2^2,
\]

(17)

where, \( l_1 = \sin \theta \cos \phi \), \( l_2 = \sin \theta \sin \phi \), \( l_3 = \cos \theta \), \( l_1 \), \( l_2 \) and \( l_3 \) the directional cosines, \( S_{ij} \) the elastic compliance constants. If the system is isotropic, the three-dimensional directional correlation is spherical. The deviation of spherical shape suggests the degree of anisotropy.

It is clear from the 3D stereoscopic pictures of bulk modulus, shear modulus, and Young’s modulus that D0\textsubscript{22}-type compounds with the same crystal structures and different compositions reveal different degree anisotropies. It can also be seen from Figure 5 that the bulk modulus of Al\textsubscript{3}La shows the strongest anisotropy. This result is consistent with the maximum anisotropy index \( A_B \) of Al\textsubscript{3}La calculated in Table 4. As proved in Figure 6, the shear modulus anisotropy of Al\textsubscript{3}La is the strongest, while that of Al\textsubscript{3}Ta is the weakest. This phenomenon is consistent with the results obtained by the anisotropy index \( A_G \) in Table 4. Finally, the anisotropic properties of Young’s modulus of these D0\textsubscript{22}-type compounds can be arranged as Al\textsubscript{3}La > Al\textsubscript{3}Zr > Al\textsubscript{3}Hf > Al\textsubscript{3}Ti > Al\textsubscript{3}Y > Al\textsubscript{3}Sc > Al\textsubscript{3}V > Al\textsubscript{3}Nb > Al\textsubscript{3}Ta, as noted in Figure 7.

Figure 5. The anisotropic characteristics of bulk modulus of the Al\textsubscript{3}TM compounds.
Figure 6. The anisotropic characteristics of shear modulus of the Al$_3$TM compounds.

Figure 7. The anisotropic characteristics of Young’s modulus of the Al$_3$TM compounds.
In particular, the projecting images of bulk modulus, shear modulus, and Young’s modulus can display the anisotropy details of the compounds more clearly, which are given in Figure 8. It should be noted that the projection features of (100) and (010) crystal planes are the same, so only the projections of (001), (010), and (110) plane are listed here. Obviously, the bulk modulus of these compounds shows greater anisotropic on the (010) and (100) planes, but it exhibits isotropy on the (001) plane. The degree of anisotropy of the same compound on (010) and (100) is the same, suggesting that the order of anisotropy is $Al_3La > Al_3Y > Al_3Sc > Al_3Zr > Al_3Nb > Al_3Ti > Al_3Hf > Al_3V > Al_3Ta$. Additionally, the shear moduli of these D0$_{22}$-type compounds are anisotropic on all three planes. Especially, the 3D diagram morphology of $Al_3La$ shear modulus anisotropy is different from that of the other eight compounds. These eight compounds have the similar anisotropy on the (001) crystal plane, while the anisotropy degree of $Al_3Ta$ displays the lowest. Furthermore, among these eight compounds, the anisotropy of $Al_3Ta$ in three crystal faces (001), (010), and (100) is smaller. Similarly, the Young’s moduli of the nine compounds are anisotropic in three planes. The degree of anisotropy of $Al_3Ti$, $Al_3V$, $Al_3Y$, $Al_3Zr$, $Al_3Nb$, $Al_3Hf$, and $Al_3Ta$ is smaller on (100) and (010) crystal planes, while that of $Al_3Sc$ and $Al_3La$ is larger on (100) and (010) crystal planes. However, it is interesting to note that the anisotropy of Young’s modulus is in the opposite direction to that of the shear modulus. Obviously, the Young’s modulus of $Al_3Ta$ is less anisotropic in all three planes, while the anisotropy of $Al_3La$ is greater.

![Figure 8](image-url)  
Figure 8. The projections of bulk modulus, shear modulus and Young’s modulus on the (001), (010), and (110) crystal planes of $Al_3TM$ compounds.
Strangely, from Figures 5–8, the anisotropic appearances of Al₃La in bulk modulus, shear modulus, and Young’s modulus is quite different from those of the other eight compounds. As discussed earlier, Al₃La has higher enthalpy of formation, lower modulus values, unique toughness, and smallest Vickers hardness. Thus, it is speculated that D0₂₂-type Al₃La may not exist.

Corresponding to Figure 8, the Table 5 summarizes more specific values of bulk modulus, shear modulus, and Young’s modulus in four directions. Due to the structural properties of D0₂₂-type compounds, the bulk modulus, shear modulus, and Young’s modulus are equal in the directions of [100] and [010]. Likewise, the bulk modulus of these compounds in the [1̅10] direction is equal to those in the [100] and [010] directions. However, the shear modulus and Young’s modulus of these compounds in the [1̅10] direction are not equal to those in the [100] and [010] directions. The maximum and minimum bulk modulus of Al₃Ta and Al₃La in [001] direction is 375.16 and 103.00 GPa, respectively. This means that Al₃Ta has the strongest resistance of compression in [001] direction. In addition, the shear modulus in the directions of [001] and [1̅10] are smaller than those in the directions of [100] and [010], which indicates stronger shear strain capacity. The maximum shear modulus of Al₃Nb in [100] and [010] direction is 117.56 GPa. Furthermore, the Young’s modulus of other compounds except Al₃Sc and Al₃La in the [001] direction is greater than that in the [100] and [010] directions. The reason is that C₃₃ value of Al₃Sc and Al₃La is smaller than C₁₁ and C₂₂, which leads to greater compressibility in c-axis direction.

| Species | B     | G     | E     |
|---------|-------|-------|-------|
| Al₃Sc   | 266.74| 266.74| 212.26| 266.74| 78.78 | 78.78 | 67.20 | 57.33 | 130.84| 130.84| 128.50| 189.79|
| Al₃Ti   | 325.45| 325.45| 297.08| 325.45| 108.13| 108.13| 94.46 | 68.53 | 151.81| 151.81| 201.28| 255.45|
| Al₃V    | 364.46| 364.46| 345.91| 364.46| 112.85| 112.85| 99.37 | 81.44 | 188.96| 188.96| 245.33| 279.07|
| Al₃Y    | 240.26| 240.26| 189.66| 240.26| 64.17 | 64.17 | 51.60 | 43.06 | 102.58| 102.58| 112.72| 168.70|
| Al₃Zr   | 321.50| 321.50| 276.17| 321.50| 104.73| 104.73| 90.00 | 64.54 | 143.97| 143.97| 188.37| 251.67|
| Al₃Nb   | 387.46| 387.46| 351.47| 387.46| 117.56| 117.56| 104.57| 88.11 | 206.57| 206.57| 255.60| 292.41|
| Al₃La   | 253.02| 253.02| 103.00| 253.02| 20.84 | 20.84 | 12.67 | 16.21 | 64.20 | 64.20 | 58.86 | 114.52|
| Al₃Hf   | 333.26| 333.26| 306.61| 333.26| 107.66| 107.66| 92.91 | 66.74 | 148.61| 148.61| 201.15| 257.63|
| Al₃Ta   | 393.05| 393.05| 375.16| 393.05| 116.16| 116.16| 104.96| 90.63 | 212.90| 212.90| 257.95| 285.91|

3.4. Electronic Structures

The compounds in present work are all D0₂₂-type compounds that are bound with transition metals. Because of their orientation-related bonding properties, it is of great significance to analyze the chemical bonding properties and electronic structures of these D0₂₂-type compounds. In Figure 9, we calculated the total density of states (TDOS) and partial density of states (PDOS) of D0₂₂-Al₃TM compounds. The vertical dashed line at zero energy shows the Fermi level (E_F). Obviously, the density of states at Fermi level is not zero, suggesting that these phases have metal properties and electrical conductivity. For Al₃Sc, Al₃Ti, Al₃V, Al₃Y, Al₃Zr, Al₃Nb, Al₃La, Al₃Hf, and Al₃Ta phases, there is a peak near the Fermi level of the TDOS curves, implying their good conductivity.

It is obvious that the TDOS at the Fermi level for Al₃Sc, Al₃Ti, Al₃V, Al₃Y, Al₃Zr, Al₃Nb, Al₃La, Al₃Hf and Al₃Ta are 3.43, 4.25, 1.99, 3.59, 3.85, 1.30, 4.65, 3.71, and 1.08 electrons/eV, respectively. The TDOS curve in Figure 9 also shows the pseudogap near E_F, which is due to the electron transfer to the low energy region. The lower the position of E_F in the gap, the more stable the structure of intermetallics is. Thus, Al₃Ta can be considered as the most stable compound. When the pseudogap is larger, it means stronger bond strength and higher deformation resistance. Compared with Al₃V, Al₃Nb, and Al₃Ta in Figure 9, it can be noted that the pseudogap of Al₃Ta has the widest gap, meaning that the covalent bond strength of Al₃Ta is stronger than that of Al₃V and Al₃Nb. This explains why Al₃Ta has...
the highest hardness. In view of nine compounds, the shapes of TDOS for Al3Sc, Al3Ti, Al3Y, Al3Zr, Al3La, and Al3Hf are similar, which demonstrate that their chemical bonds are similar. The TDOS curves of Al3V, Al3Nb, and Al3Ta are alike, which is to say that the V-shaped tip intersects the dotted line of Fermi level.

Figure 9. Total and partial electronic densities of states near Fermi level of Al3TM compounds.

The PDOS curves clearly show that the contribution of Al-s on the surface of Fermi level is small, which is mainly contributed by the Al-p state. The Fermi level of TDOS is mainly formed by the strong hybridization of Al-p and TM (TM = Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta)-d states. Obviously, the hybridization of Al-s and TM (TM = Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta)-s states are less helpful for the Fermi level of TDOS. The obtained quantity of bonding electrons per atom between −13 eV and Fermi level is 3.005, 3.243, 3.493, 3.003, 3.242, 3.499, 2.997, 3.247, and 3.501 for Al3Sc, Al3Ti, Al3Y, Al3V, Al3Zr, Al3Nb, Al3La, Al3Hf and Al3Ta, respectively.

Meanwhile, in order to explore the chemical bonds and charge transfer in all D022-type compounds, the charge density difference on the (010) basal plane of these compounds were considered. In Figure 10, the distribution state of charge density difference of Al3Sc, Al3Ti, Al3V, Al3Y, Al3Zr, Al3Nb, Al3La, Al3Hf, and Al3Ta can be seen clearly. The values of charge density difference map are plotted from −0.04 to 0.04 e/Å³. Besides, the red and blue mean separately the aggregation and reduction of electrons.
As can be seen from the Figure 10, there are electron deletions around both Al and TM atoms (blue), and electron aggregation between Al and TM atoms (red). This suggests that the electrons are aggregated into a covalent Al-TM bond between the atoms Al and TM. Similarly, there is a large amount of charge accumulation between Al and Al atoms, indicating that the Al-Al bond in the compound has covalent bond characteristics. Furthermore, a larger degree of localization of electrons reflects a stronger bond. Consequently, the electron concentration between the Al and TM (V, Nb and Ta) atoms in Al3V, Al3Nb and Al3Ta compounds is higher, which leads to the conclusion that Al-TM (V, Nb and Ta) bonds are stronger. On the contrary, it can be suggested that the bonds of Al-La and La-La are the weakest, which is because the less the localization degree of electrons, the weaker the bonds are.

3.5. Work Function

In order to further understand the properties of D0₂₂-type compounds in this study, some surface work functions were calculated. Theoretically, the work function is the energy barrier used to move electrons from the surface of solid compounds to the free space, as noted by the following expression [47,48]:

$$\varphi = V_{\text{vac}} - E_F$$  \hspace{1cm} (18)

where $\varphi$ is work function, and symbol $V_{\text{vac}}$ means the electrostatic potential of the vacuum region near the surface. $E_F$ corresponds to the Fermi energy of the slab. The schematic diagram of the electronic movement is presented in Figure 11. When a compound has a higher electron work function, it takes more energy to change its electron state. Therefore, there are greater obstacles to improving the state or properties of compounds such as mechanical and elastic properties. The higher electron work function of the compound indicates that it has stronger atomic bond [49,50]. In present work, the work function value of Al3Sc, Al3Ti, Al3V, Al3Y, Al3Zr, Al3Nb, Al3La, Al3Hf, and Al3Ta is 3.838, 4.305, 4.206, 3.754, 3.953, 4.100, 3.291, 4.079, and 4.078 eV on (100) plane, respectively. It is found that the value of Al3La is the smallest. Therefore, the Young’s modulus and Vickers hardness of Al3La are the lowest, which is consistent with the previous calculated results.

![Figure 10. The electron density difference of Al₃TM compounds.](image-url)
The SEM, XRD, and stress-strain curves of CoCrFeAlTa

3.6. Experimental Design

Figure 12a shows the SEM and XRD images of representative CoCrFeAlTa0.16 HEA at 50 h annealing state. It is obvious that the alloy exhibits the crystal structure of FCC. The grain distribution in the image is clearly angular. The typical stress-strain curves of the solid solution and different heat treatment states can be seen in Figure 12b. It can be observed that the strength and toughness of the sample is better when it is treated at 700 °C/50 h. However, the strength and toughness of the samples were reduced when they were treated for 700 °C/100 h. It is possible that the grain size will be further enlarged as the solution time increases. In fact, the specimen annealed for 50 h will have D0$_{22}$-type Al$_3$Ta phase, resulting in its tensile strength up to 1120 MPa and elongation up to 26%. This result fully reflects the strengthening effect of Al$_3$Ta phase.

![Figure 11](image1.png)  
**Figure 11.** The schematic diagram of the electronic movement related to work function.

![Figure 12](image2.png)  
**Figure 12.** The SEM, XRD, and stress-strain curves of CoCrFeAlTa$_{0.16}$. (a) The SEM and XRD images at 50 h annealing state; (b) The stress-strain curves of different heat treatment states.
In order to more clearly characterize the microstructure of D0\textsubscript{22}, Figure 13 exhibits the TEM structure of Al\textsubscript{3}Ta phase. According to the image, the Al\textsubscript{3}Ta phase is needle like and has a certain orientation. It presents a crystallographic relationship with the matrix, [001]\textsubscript{D0\textsubscript{22}}//[001]\textsubscript{Matrix}. The diffraction pattern in Figure 13b clearly illustrates this relationship. It can see that plane (2\overline{2}0) of the matrix corresponds to plane (110) of D0\textsubscript{22}-type Al\textsubscript{3}Ta phase. Moreover, stereographic projection of the orientation relationship denotes the crystal plane correspondence between the two phases more clearly, as shown in Figure 13c,d. This orientation relationship further indicates that the formation of Al\textsubscript{3}Ta contributes to the improvement of its strength and toughness. Therefore, the reliability of the simulation is further confirmed by the experiments, which has important reference values for the design and application of this material.

![Figure 13](image)

**Figure 13.** The TEM structure of D0\textsubscript{22}-Al\textsubscript{3}Ta phase. (a) the morphology of D0\textsubscript{22}-Al\textsubscript{3}Ta phase; (b) the diffraction pattern of D0\textsubscript{22}-Al\textsubscript{3}Ta phase; (c) the stereographic projection of the matrix; (d) the stereographic projection of D0\textsubscript{22}-Al\textsubscript{3}Ta phase.

### 4. Conclusions

Overall, first principles calculations have been performed on elastic anisotropy, electronic structures, and work function of D0\textsubscript{22}-type Al\textsubscript{3}TM (TM = Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta), including Al\textsubscript{3}Sc, Al\textsubscript{3}Ti, Al\textsubscript{3}V, Al\textsubscript{3}Y, Al\textsubscript{3}Zr, Al\textsubscript{3}Nb, Al\textsubscript{3}La, Al\textsubscript{3}Hf, and Al\textsubscript{3}Ta, respectively. The obtained results agree with the existing theoretical values.

It is noted that the thermodynamic properties of the nine D0\textsubscript{22}-type compounds are stable. The alloying ability of the nine D0\textsubscript{22}-type compounds from strong to weak can be arranged as Al\textsubscript{3}Zr > Al\textsubscript{3}Nb > Al\textsubscript{3}Hf > Al\textsubscript{3}Ti > Al\textsubscript{3}Sc > Al\textsubscript{3}Ta > Al\textsubscript{3}Y > Al\textsubscript{3}V > Al\textsubscript{3}La. The order of the bulk modulus of these D0\textsubscript{22}-type compounds is Al\textsubscript{3}Ta > Al\textsubscript{3}Nb > Al\textsubscript{3}V > Al\textsubscript{3}Hf.
> Al₃Ti > Al₃Zr > Al₃Sc > Al₃Y > Al₃La. Specifically, Al₃Ta and Al₃La have the largest shear modulus (108.19 GPa) and smallest one (22.41 GPa) separately. It can be found that Al₃Ta and Al₃La have the largest Young’s modulus (254.17 GPa) and smallest one (59.62 GPa). It is evident that Al₃Ta has the higher hardness and is not easy to deform.

Furthermore, the universal anisotropy of these D₀₂₂-type compounds can be listed as Al₃La > Al₃Zr > Al₃Hf > Al₃Ti > Al₃Y > Al₃Sc > Al₃V > Al₃Nb > Al₃Ta. The Al₃La and Al₃Ta have the highest and lowest Aᵥ values, demonstrating that the shear modulus anisotropy of Al₃La is the strongest, while that of Al₃Ta is the weakest. The A₃ value of Al₃La has the most deviation from 1, indicating that the Al₃La shows the highest shear anisotropy in the (001) plane. Except for Al₃Sc and Al₃La, the Young’s modulus of other compounds in [001] direction is greater than that in [100] and [010] directions. From the standpoint of anisotropy, it is speculated that D₀₂₂-type Al₃La may not exist.

It can be suggested that the density of states at Fermi level is not zero, suggesting that these phases have metal properties and electrical conductivity. Obviously, the pseudogap of Al₃Ta has the widest width, meaning that the covalent bond strength of Al₃Ta is stronger than that of Al₃V and Al₃Nb. The electron concentration between the Al and TM (V, Nb and Ta) atoms in Al₃V, Al₃Nb and Al₃Ta compounds is higher, which shows that Al-TM (V, Nb and Ta) bonds are stronger. Ultimately, the work function of Al₃La is the smallest on (100), demonstrating that the Young’s modulus and Vickers hardness of Al₃La are the lowest.

Based on the calculated results, a kind of D₀₂₂ reinforced alloy was designed, which proves that this phase has an excellent strengthening effect. The matrix is strengthened by D₀₂₂-type Al₃Ta phase, resulting in its tensile strength up to 1120 MPa and elongation up to 26%. The crystallographic relationship between D₀₂₂-type Al₃Ta phase and matrix is [001]D₀₂₂ // [001]Matrix. The experimental results of this work further verify the reliability of the calculated results, which has important reference values for the design and application of the materials.

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