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Effects of Doped Elements (Si, Cr, W and Nb) on the Stability, Mechanical Properties and Electronic Structures of MoAlB Phase by the First-Principles Calculation

Yongxin Jian ^{1,*} , Zhifu Huang ^{1,*}, Yu Wang ² and Jiandong Xing ¹

¹ State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China; jiandongxing@xjtu.edu.cn

² Shaanxi Special Equipment Inspection and Testing Institute, Xi'an 710048, China; yuwang@stu.xjtu.edu.cn

* Correspondence: yxjian@xjtu.edu.cn (Y.J.); zhifuhuang@xjtu.edu.cn (Z.H.)

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Abstract: First-principles calculations based on density functional theory (DFT) have been performed to explore the effects of Si, Cr, W, and Nb elements on the stability, mechanical properties, and electronic structures of MoAlB ternary boride. The five crystals, with the formulas of $\text{Mo}_4\text{Al}_4\text{B}_4$, $\text{Mo}_4\text{Al}_3\text{SiB}_4$, $\text{Mo}_3\text{CrAl}_4\text{B}_4$, $\text{Mo}_3\text{WAl}_4\text{B}_4$, and $\text{Mo}_3\text{NbAl}_4\text{B}_4$, have been respectively established. All the calculated crystals are thermodynamically stable, according to the negative cohesive energy and formation enthalpy. By the calculation of elastic constants, the mechanical moduli and ductility evolutions of MoAlB with elemental doping can be further estimated, with the aid of B/G and Poisson's ratios. Si and W doping cannot only enhance the Young's modulus of MoAlB, but also improve the ductility to some degree. Simultaneously, the elastic moduli of MoAlB are supposed to become more isotropic after Si and W addition. However, Cr and Nb doping plays a negative role in ameliorating the mechanical properties. Through the analysis of electronic structures and chemical bonding, the evolutions of chemical bondings can be disclosed with the addition of dopant. The enhancement of B-B, Al/Si-B, and Al/Si-Mo bondings takes place after Si substitution, and W addition apparently intensifies the bonding with B and Al. In this case, the strengthening of chemical bonding after Si and W doping exactly accounts for the improvement of mechanical properties of MoAlB. Additionally, Si doping can also improve the Debye temperature and melting point of the MoAlB crystal. Overall, Si element is predicted to be the optimized dopant to ameliorate the mechanical properties of MoAlB.

Keywords: MoAlB phase; elemental doping; mechanical properties; electronic structures; first-principles calculations

1. Introduction

Binary transition metal borides are regarded as the superior candidates for high-temperature structural ceramics, due to their outstanding properties, such as high melting temperature, high hardness, and thermodynamic stability [1–3]. However, the inherent brittleness, poor oxidation resistance, as well as low damage tolerance have impeded the application of binary borides. To address these limitations, the researchers have tried to introduce an Al atomic layer into transition metal borides to form so-called MAB phases [4,5]. In MAB phases, single or double Al atomic layers are interleaved into a transition metal boride sublattice. The structures of MAB phases are analogous to the previous MAX phases, which show significant advantages for both metal and ceramics with good heat and electricity conduction, and considerable ductility and damage tolerance [6–10]. In this case, MAB phases are also expected to possess the excellent properties of both metals and borides.

Jeitschko et al. [4] first discovered MAIB (space group Cmmm) ternary transition metal borides in 1966. Subsequently, extensive research has focused on the synthesis of single crystal ternary borides, and determining their crystal structures [11]. In 2016, Kota et al. [5,12] synthesized the polycrystalline MoAlB bulk by a hot-pressing method, and investigated its oxidation resistance, heat and electrical conductivity, thermal expansion, and mechanical properties. Their results suggest the significant potential of MoAlB ceramic in application to high-temperature fields. Afterwards, researchers all over the world conducted extensive investigations on the synthesized methods, mechanical properties, thermal shock behaviors, oxidation behaviors, as well as the friction and wear behaviors of MoAlB ceramics [12–24]. As reported, MoAlB exhibited excellent high-temperature oxidation resistance and compressive properties, but the fracture toughness was still insufficient, especially considering its potential application as structural parts. In spite of the introduction of Al atomic layer, the MoAlB phase still fails in its brittleness, by way of cleavage fractures. In this case, addressing the problem of the intrinsic brittleness of MoAlB is of great significance for its industrial application.

Traditionally, the elemental doping method is usually executed to ameliorate the mechanical properties of metallic materials as well as intermetallics (for instance carbides and borides) [25–30]. Jian et al. [29,31] improved the fracture toughness of Fe₂B without sacrificing the hardness by appropriate Cr or Mn addition. Shen et al. [32] managed to enhance the hardness and flexure strength of Mo₂FeB₂ ceramic with Cr dopant. For MoAlB, Shigeru et al. [33] tried to investigate the effects of the transition metal atoms (Cr, W, V, and Nb et al.) on the hardness and oxidation resistance of MoAlB. In their study, only (Mo_xCr_{1-x})AlB and (Mo_xW_{1-x})AlB were successfully obtained by the flux method using molten aluminum as the solvent, and W was found to play a positive role in improving the hardness. However, the intrinsic reason for the mechanical evolution originating from elemental doping was not clarified deeply. Recently, Ma et al. [34] found that Si addition can facilitate the formation of MoAl_{1-x}Si_xB so as to improve the strength and hardness of MoAlB. Similarly, the strengthening mechanism by Si doping was substantially not discussed in their work. Thus, the affecting mechanism of elemental doping on MoAlB phase urgently needs to be clarified, which can also help to find new strategies to ameliorate the mechanical properties, especially for the toughness.

In recent years, first-principles calculation based on density functional theory (DFT) has shown considerable accuracy in predicting the phase stability, lattice parameters, mechanical properties, and electronic structures of compounds [35–38]. Thus, theoretical calculation has developed to be an effective tool to predict and design new compounds with extraordinary properties. Simultaneously, the abundant information from calculations can help to disclose the intrinsic reason, which cannot be observed through experimental methods. In this case, this work mainly focuses on systematically investigating the effects of Si, Cr, W, and Nb doping on the stability, elastic, and physical properties of MoAlB. By analyzing the evolutions of the electronic structures and bonding characters, the affecting mechanism has been discussed comprehensively. In this case, this work is expected to provide guideline for improving the mechanical properties of MoAlB ceramic, by way of element doping.

2. Methodology

In this work, the calculations were performed by using density functional theory (DFT) implemented in the Cambridge Serial Total Energy Package (CASTEP) code [39,40]. The exchange correlation energy was treated according to the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) [41,42]. Ultrasoft pseudopotentials were employed to describe the interactions between the ionic core and valence electrons in the reciprocal space [43]. The plane wave energy cutoff was fixed at 600 eV. Brillouin zone sampling was conducted by Monkhorst–Pack method, with the special k-point mesh of 10 × 10 × 10. The crystal was fully optimized by modifying the lattice parameters and internal atomic positions using the Broyden–Fletcher–Goldfarb–Shannon (BFGS) minimization scheme [44]. The total energy of the lattice structure was minimized to converge to 5 × 10^{−6} eV/atom, along with the ionic Hellmann–Feynman force components, ionic displacements, and stress tensor components being converged to within 0.01 eV/Å, 5 × 10^{−4} Å, and 0.02 GPa, respectively.

Figure 1a illustrates the crystal cell of initial MoAlB, with an orthorhombic lattice structure. Mo, Al, and B atoms occupy the 4c Wyckoff positions of the $Cmcm$ space group [11]. In this research, the crystal model of Si doped MoAlB was established by replacing one Al atom by Si, considering the similar atomic radius, as shown in Figure 1b. However, given the similarity among Cr, W, Nb, and Mo, the crystal structure of X (X representing Cr, W, or Nb) doped MoAlB was obtained with one X atom occupying the initial Mo position [45]. The crystal structure of X doped MoAlB is shown in Figure 1c. In this case, five crystals with the formulas of $Mo_4Al_4B_4$, $Mo_4Al_3SiB_4$, $Mo_3CrAl_4B_4$, $Mo_3WAl_4B_4$, and $Mo_3NbAl_4B_4$ were investigated in this work, involving the stability, mechanical properties, electronic structures, and thermal properties.

Figure 1. Crystal structures of MoAlB: (a) Initial MoAlB (bond distance unit: Å); (b) Si doped MoAlB; (c) X doped MoAlB.

3. Results and Discussion

3.1. Equilibrium Structure and Stability

After full optimization, the calculated lattice parameters of the five crystal structures are shown in Table 1. Compared with experimental results, the theoretical results of MoAlB in this work show great agreement, with the deviations less than 0.56% [5,46]. In addition, the results in this work are highly consistent with the reported theoretical results calculated with the same method [47]. Thus, the calculating method and parameters implemented in this work are supposed to be suitable, which ensures highly accurate predictions of other doped crystals. From Table 1, it can be found that the volume of crystal cell shrunk after adding Si and Cr, while it tended to swell with the addition of W and Nb. This phenomenon can be easily understood considering the deviations between the doped atom and the initial one. In addition, Cr doped MoAlB crystal shows the lowest density, which decreases by 5.7% compared with the non-doping MoAlB. On the contrary, W doping dramatically increases the density of MoAlB by about 16.4%.

Table 1. The calculated lattice parameters, density, cohesive energy, and formation enthalpy.

Cell Formula	Lattice Parameters (Å)			Vol (Å ³)	ρ (g/cm ³)	E_{coh} (eV/atom)	ΔH_f (eV/atom)
	<i>a</i>	<i>b</i>	<i>c</i>				
Mo ₄ Al ₄ B ₄	3.214	14.038	3.110	140.292	6.332	−7.628	−0.449
	3.210 [5]	13.980 [5]	3.100 [5]	—	—	—	—
	3.200 [46]	13.960 [46]	3.100 [46]	—	—	—	—
	3.216 [47]	14.062 [47]	3.103 [47]	—	—	—	—
Mo ₄ Al ₃ SiB ₄	3.211	13.766	3.122	138.016	6.449	−7.746	−0.426
Mo ₃ CrAl ₄ B ₄	3.172	13.977	3.080	136.586	5.969	−7.503	−0.416
Mo ₃ WAl ₄ B ₄	3.216	14.024	3.112	140.334	7.370	−7.633	−0.412
Mo ₃ NbAl ₄ B ₄	3.226	14.194	3.129	143.283	6.164	−7.590	−0.477

Thermostability of the crystal is an important parameter in evaluating the possibility of the doping reaction, and can be estimated by the parameters of cohesive energy (E_{coh}) and formation enthalpy (ΔH_f). In general, negative values of E_{coh} and ΔH_f indicate the crystal structure to be thermodynamically stable. The E_{coh} and ΔH_f of a compound can be calculated according to Equations (1) and (2) [48–51]:

$$E_{coh}(A_xB_yC_zD_m) = \frac{E_{tol}(A_xB_yC_zD_m) - xE_{iso}(A) - yE_{iso}(B) - zE_{iso}(C) - mE_{iso}(D)}{x + y + z + m} \quad (1)$$

$$\Delta H_f(A_xB_yC_zD_m) = \frac{E_{tol}(A_xB_yC_zD_m) - xE_{bulk}(A) - yE_{bulk}(B) - zE_{bulk}(C) - mE_{bulk}(D)}{x + y + z + m} \quad (2)$$

where E_{tol} represents for total energy; E_{iso} and E_{bulk} represent the energy of an isolated atom and a single atom in bulk state, respectively. From Table 1, it can be concluded that the all five calculated crystal structures are thermodynamically stable in view of the negative values of E_{coh} and ΔH_f . From the perspective of E_{coh} , Si doped MoAlB is the most stable crystal due to its smallest E_{coh} , and the stability of crystal structures can be ranked in the order, Mo₄Al₃SiB₄ > Mo₃WAl₄B₄ > Mo₄Al₄B₄ > Mo₃NbAl₄B₄ > Mo₃CrAl₄B₄. On the other hand, the negative formation enthalpies also prove all the crystals structures to be thermodynamically stable. In this context, it can be concluded that the doping of Si, Cr, W, and Nb should be realized in experiments.

3.2. Elastic Properties

The mechanical properties can be investigated by calculating the elastic constants of the crystals. In this work, the elastic constants have been evaluated by the stress-strain method, where the stress-strain curve was described by generalized Hooker's law, as shown in Equation (3):

$$\sigma_{ij} = C_{ijkl}\epsilon_{ij} \quad (3)$$

where σ_{ij} represents for the stress tensor; ϵ_{ij} and C_{ijkl} represent the Lagrangian strain tensor and elastic constant tensor, respectively. The elastic constants (C_{ij}) of all the five crystals have been calculated and listed in Table 2. The second order elastic constants of MoAlB show pretty good agreement with the reported results [37,47], indicating the reliability of our calculation. The mechanical stability of compounds can be justified according to Boron–Huang's criteria [52–54]. For the MoAlB crystals with orthorhombic lattice, the general criteria can be expressed as Equation (4):

$$\begin{aligned} C_{11}C_{12} - C_{21}^2 &> 0; C_{22}C_{33} - C_{23}^2 > 0; C_{33}C_{11} - C_{31}^2 > 0; \\ C_{11}C_{22}C_{33} + 2C_{12}C_{23}C_{31} - C_{11}C_{23}^2 - C_{22}C_{31}^2 - C_{33}C_{12}^2 &> 0; \\ C_{ij} &> 0 (i = j = 1 \sim 6) \end{aligned} \quad (4)$$

Table 2. Elastic constants of MoAlB crystals with, and without, doping (GPa).

Species	C ₁₁	C ₁₂	C ₁₃	C ₂₂	C ₂₃	C ₃₃	C ₄₄	C ₅₅	C ₆₆
Mo ₄ Al ₄ B ₄	348.66	140.80	150.45	322.30	121.32	398.32	193.60	159.73	176.43
Mo ₄ Al ₃ SiB ₄	357.48	150.87	149.71	351.81	134.92	393.61	191.41	162.74	176.75
Mo ₃ CrAl ₄ B ₄	341.88	139.62	139.42	304.52	124.98	393.80	190.72	157.27	173.26
Mo ₃ WAl ₄ B ₄	350.73	143.95	154.20	333.69	124.09	400.90	194.74	162.60	177.49
Mo ₃ NbAl ₄ B ₄	326.66	138.54	145.38	297.68	125.97	374.18	185.88	162.37	186.67

According to the constants in Table 2, all five crystal structures are mechanically stable, as they fully satisfy the above stability criterion. Like the MAX phases, the C₁₁, C₂₂, and C₃₃ of MoAlB crystal, representing elastic stiffness against principal strain, are much higher than those against shear strains (C₄₄, C₅₅ and C₆₆). In other words, MoAlB crystal is considerably incompressible along *a*, *b*, and *c* crystal axis, but shows relatively weaker resistance to the shear deformation on the (1 0 0), (0 1 0) and (0 0 1) planes. Furthermore, it can be observed that C₁₁ and C₃₃ are higher than C₂₂ for all five crystals, indicating that MoAlB is more incompressible along the *a* and *c* axes [38]. The weaker incompressibility along the *b* axis may be attributed to the double-layer Al. C₃₃ is the largest among all the elastic constants, which signifies the strongest covalent bonding along the *c* axis. Compared with initial MoAlB, Si and W doping are beneficial to improving the incompressibility along the *a* and *c* axes, with the increase of C₁₁ and C₃₃. On the other hand, it is apparent that the resistance to shear on the (0 1 0) plane is the weakest considering the smallest C₅₅ value. However, the (1 0 0) plane is expected to show the strongest resistance to shear. Intrinsically, the elastic properties are mainly responding to the chemical bonding in the crystal, which will be deeply discussed thereafter.

The ductility and brittleness of a compound can be verified by the value of Cauchy pressure on some extent [38]. If the Cauchy pressure is negative, the compound is expected to be brittle in nature. According to Table 2, Cauchy pressure of each calculated crystal can be calculated by the equation of (C₁₂–C₄₄). It can be deduced from the negative Cauchy pressures that the calculated MoAlB crystals are intrinsically brittle. Furthermore, the ductility relation is Mo₄Al₃SiB₄ > Mo₃NbAl₄B₄ > Mo₃WAl₄B₄ > Mo₃CrAl₄B₄ > Mo₄Al₄B₄, by comparing the values of Cauchy pressure. In this context, it can be concluded that the addition of Si, Nb, W, and Cr benefits the improved ductility of MoAlB.

The bulk modulus (*B*), shear modulus(*G*), and Young's modulus(*E*) can be estimated based on the elastic constants (*C_{ij}*), according to the Voigt–Reuss–Hill (VRH) scheme [55]. The VRH approximation means the average of Voigt and Reuss approximations. Herein, Voigt approximation, based on the assumption of uniform strain, decides the upper bounds of the elastic modulus, as expressed by Equations (5) and (6):

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{23} + C_{13}) \quad (5)$$

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33}) - \frac{1}{15}(C_{12} + C_{23} + C_{13}) + \frac{1}{5}(C_{44} + C_{55} + C_{66}) \quad (6)$$

And Reuss approximation, based on the assumption of uniform stress, decides the lower bounds. It can be defined as the elastic compliances (*S_{ij}*) which are the inverse matrix of *C_{ij}*, as expressed by Equations (7) and (8):

$$\frac{1}{B_R} = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{13}) \quad (7)$$

$$\frac{1}{G_R} = \frac{4}{15}(S_{11} + S_{22} + S_{33}) - \frac{4}{15}(S_{12} + S_{23} + S_{13}) + \frac{1}{5}(S_{44} + S_{55} + S_{66}) \quad (8)$$

Finally, the *B*, *G*, and *E* can be obtained following Equations (9)–(11), and Poisson's ratio (*ν*) can be calculated according to Equation (12).

$$B = \frac{1}{2}(B_V + B_R) \quad (9)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (10)$$

$$E = \frac{9BG}{3B + G} \quad (11)$$

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (12)$$

Table 3 lists the calculated bulk moduli (B), shear moduli (G), and Young's moduli (E) of all five calculated crystals. Additionally, the moduli data at 300K, measured by high-temperature resonant ultrasound spectroscopy (RUS) by Kota et al., have been provided as a comparison [56]. As shown, the calculated E of MoAlB is a little underestimated in this work compared with the experimental result. The calculated bulk modulus, shear modulus, and Young's modulus have been plotted in Figure 2a. First, it can be found that Young's moduli of MoAlB are considerably higher, with the values larger than 350 GPa indicating the strong chemical bonding inside the crystal. From Figure 2a, it can be visibly observed that the bulk modulus (B) is substantially larger than the shear modulus (G). Intriguingly, Si and W doped MoAlB exhibits a relatively higher elastic moduli compared to the others. This implies Si and W doping can help enhance the bonding interactions among the atoms. However, Cr and Nb doping seem to be detrimental to the elastic moduli. On the other hand, Pugh's ratio can be obtained by calculating the ratio of B/G . B/G ratio is usually used to judge the ductile and brittle character of a solid [57]. A higher B/G value indicates a higher ductility, with a critical value of 1.75. Thus, the five calculated MoAlB crystals can be classified as brittle materials, with a B/G value less than 1.75, which is totally consistent with the prediction from Cauchy pressure. However, according to the previously reported experimental results [5,14,17,22], MoAlB exhibits considerable toughness and damage tolerance. In this case, the predication about the toughness of MoAlB may not be so dependent as other compounds on the value the of B/G ratio. This phenomenon agrees well with the literature's reports that Pugh's ratio may not necessarily be a strong indication of ductility, for the ternary layered compounds, such as MAB and MAX phases [36,58,59], because the effects of the layered structure, and significantly weak bonds of Al, on ductility, are underestimated during the calculation. Figure 2b reveals the Poisson's and B/G ratios of the calculated MoAlB crystals. As shown, Mo₄Al₃SiB₄ crystal possesses the highest B/G and Poisson's ratios, indicating superior ductility. By comparison, it can be concluded that Si and W doping can play a positive role in improving the ductility of MoAlB, while Cr and Nb doping seem to make adverse contributions.

Table 3. The elastic moduli (GPa), Poisson's ratios, and B/G ratios (dimensionless).

Species	B_V	B_R	B_{VRH}	G_V	G_R	G_{VRH}	E	ν	B/G
Mo ₄ Al ₄ B ₄	210.49	208.67	209.58 232.90 [56]	149.73	140.04	144.89 151.20 [56]	353.26 372.90 [56]	0.219	1.446
Mo ₄ Al ₃ SiB ₄	219.32	218.94	219.13	150.67	142.18	146.42	359.25	0.227	1.497
Mo ₃ CrAl ₄ B ₄	205.36	203.29	204.33	146.66	136.31	141.49	344.86	0.219	1.444
Mo ₃ WAl ₄ B ₄	214.42	212.99	213.71	151.17	141.54	146.35	357.46	0.221	1.460
Mo ₃ NbAl ₄ B ₄	202.03	200.13	201.08	146.23	132.79	139.51	339.91	0.218	1.441

Figure 2. Mechanical properties of MoAlB crystals: (a) elastic moduli; (b) B/G and Poisson's ratios.

Poisson's ratio is also one of the important parameters in assessing the solid's ductility and brittleness. With the critical value of 0.26, the material with a Poisson's ratio lower than this usually behaves in a brittle manner, otherwise the material is expected to be ductile. In this context, the five calculated MoAlB crystals are all classified as brittle materials. This shows great consistency with the results of Cauchy's pressure and B/G ratio. Moreover, the variation of Poisson's ratio is also in good agreement with the B/G ratio. In summary, Si and W doping can enhance the elastic moduli and improve the ductility of MoAlB, which is expected to be an effective method to optimize the mechanical properties.

3.3. Elastic Anisotropy

The anisotropy of mechanical properties is a key factor that affects the material's properties. Microcracks usually appear, originating from the mechanical anisotropy of materials. In MoAlB crystal, the elastic modulus along different principal axes are expected to differ from each other, considering the difference in the elastic constants in Table 2. To reveal the anisotropic features, the universal anisotropic index (A^U), percent anisotropies (A^B and A^G), and shear anisotropic indexes (A_1 , A_2 and A_3) have been calculated in this work according to Equations (13)–(18):

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0 \quad (13)$$

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (14)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (15)$$

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \text{ for (100) plane} \quad (16)$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \text{ for (010) plane} \quad (17)$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \text{ for (001) plane} \quad (18)$$

Table 4 lists the calculated anisotropic indexes of MoAlB crystals, with and without elemental doping. First, it can be found that $\text{Mo}_4\text{Al}_3\text{SiB}_4$ and $\text{Mo}_3\text{WAl}_4\text{B}_4$ have relatively smaller A^U , compared with the initial MoAlB, implying that the crystals tend to be more isotropic after Si and W doping. In addition, the A_B and A_G show the same varying trend with Si and W addition. Generally, directional covalent bonding plays a significant role in affecting the crystal's anisotropy,

while the metallic bonding contributes to improving the isotropy. Thus, it can be hypothesized that Si and W doping can help ameliorate the metallic character of MoAlB, which is beneficial to the crystal's ductility. This results in good agreement with the Pugh's and Poisson's ratios discussed above. Then, A_1 , A_2 , and A_3 reveal the anisotropies of shear moduli on the (1 0 0), (0 1 0), and (0 0 1) planes, respectively. $\text{Mo}_3\text{CrAl}_4\text{B}_4$ shows the smallest A_1 and $\text{Mo}_4\text{Al}_3\text{SiB}_4$ shows the smallest A_3 , while $\text{Mo}_3\text{WAl}_4\text{B}_4$ and $\text{Mo}_4\text{Al}_4\text{B}_4$ share the smallest A_2 . In other words, $\text{Mo}_3\text{CrAl}_4\text{B}_4$, $\text{Mo}_4\text{Al}_3\text{SiB}_4$, $\text{Mo}_3\text{WAl}_4\text{B}_4$, and $\text{Mo}_4\text{Al}_4\text{B}_4$ have the most isotropic shear moduli on the (1 0 0), (0 0 1), and (0 1 0) planes, respectively. Overall, $\text{Mo}_3\text{NbAl}_4\text{B}_4$ is regarded as the most anisotropic crystal due to the relatively high anisotropic index.

Table 4. The calculated anisotropic indexes of MoAlB crystals (dimensionless).

Species	A_1	A_2	A_3	A^U	A_B	A_G
$\text{Mo}_4\text{Al}_4\text{B}_4$	1.736	1.337	1.813	0.355	0.435%	3.344%
$\text{Mo}_4\text{Al}_3\text{SiB}_4$	1.695	1.369	1.735	0.301	0.089%	2.901%
$\text{Mo}_3\text{CrAl}_4\text{B}_4$	1.670	1.403	1.887	0.390	0.505%	3.658%
$\text{Mo}_3\text{WAl}_4\text{B}_4$	1.757	1.337	1.790	0.347	0.334%	3.291%
$\text{Mo}_3\text{NbAl}_4\text{B}_4$	1.813	1.547	2.150	0.516	0.474%	4.817%

Young's modulus is an important parameter to evaluate the mechanical properties of a material. Thus, the anisotropic features of Young's modulus are worthwhile to be clearly elucidated. The spatial surface contours are practical and visible, giving insight to the anisotropies of Young's modulus [37]. In this case, the spatial surface contours of Young's moduli, as a function of direction, have been depicted according to Equation (19):

$$\frac{1}{E} = l_1^4 S_{11} + l_2^4 S_{22} + l_3^4 S_{33} + 2l_1^2 l_2^2 S_{12} + 2l_1^2 l_3^2 S_{13} + 2l_2^2 l_3^2 S_{23} + l_1^2 l_3^2 S_{44} + l_1^2 l_3^2 S_{55} + l_1^2 l_2^2 S_{66} \quad (19)$$

where l_1 , l_2 , and l_3 are the directional cosines; S_{ij} represents the elastic compliance constant. In spherical coordinates: $l_1 = \sin \theta \cos \psi$, $l_2 = \sin \theta \sin \psi$ and $l_3 = \cos \theta$, respectively. Figure 3 exhibits the three-dimensional surface contours of Young's modulus of the five calculated crystals. As seen, the Young's modulus of MoAlB shows great anisotropy, because the isotropic crystal usually has a spherical contour shape. The Young's modulus of the five calculated crystals is the largest along the [1 1 1] crystal direction. On the contrary, the Young's modulus seems to be the smallest along the [0 1 0] crystal direction. Overall, the contour shapes of the five crystals have considerable similarity, which may be attributed to the small difference in their lattice structures. To clarify the differences on different feature crystallographic planes, the planar projections on the (1 0 0), (0 1 0), (0 0 1), and (1 1 0) planes have been depicted in Figure 4. It can be noticed that the Young's moduli on the (1 0 0) and (0 1 0) planes are obviously more anisotropic than those on the other two planes. Compared with the initial MoAlB crystal, the $\text{Mo}_4\text{Al}_3\text{SiB}_4$ and $\text{Mo}_3\text{WAl}_4\text{B}_4$ show more isotropic Young's modulus distribution, while the distributions of $\text{Mo}_3\text{CrAl}_4\text{B}_4$ and $\text{Mo}_3\text{NbAl}_4\text{B}_4$ are more anisotropic. This result agrees well with the discussion on the anisotropic parameter, A^U . On the other hand, it can be observed that, for five calculated crystals, the Young's moduli along the [1 1 1] direction are the largest, while those along [0 1 0] are the smallest. Along the [1 1 1] direction, the Young's modulus is higher than 400 GPa, indicating the superior stiffness. As for the three principal axes, the relationship of Young's modulus is $E_{[0 0 1]} > E_{[1 0 0]} > E_{[0 1 0]}$, which is consistent with the spatial contours in Figure 3. Furthermore, it can be found that Si and W doping can account for the enhancement of Young's modulus, especially along the [0 1 0] direction. The Young's modulus along [0 1 0] can be improved from 254.60 to 272.74 and 263.68 GPa after Si and W doping, respectively. In general, the low Young's modulus relates tightly with poor energy. Thus, Si and W doping are supposed to improve the uniaxial tension resistance along [0 1 0] of MoAlB.

Figure 3. The spatial surface contours of Young's modulus: (a) $\text{Mo}_4\text{Al}_4\text{B}_4$; (b) $\text{Mo}_4\text{Al}_3\text{SiB}_4$; (c) $\text{Mo}_3\text{CrAl}_4\text{B}_4$; (d) $\text{Mo}_3\text{WAl}_4\text{B}_4$; (e) $\text{Mo}_3\text{NbAl}_4\text{B}_4$.

Figure 4. Planar projections of the Young's modulus (GPa) on different planes: (a) on the (1 0 0) plane; (b) on the (0 1 0) plane; (c) on the (0 0 1) plane; (d) on the (1 1 0) plane.

3.4. Electronic Structures

To further put insight into the bonding character of MoAlB, as well as the elementally doped crystals, the electronic structures were explored, including the density of states (DOS) and electron density distribution. Figure 5 illustrates the total density of states (TDOS) and the partial density of states (PDOS) of the five calculated crystals. For all five crystals, the values of the DOS, at Fermi energy level (E_f), are larger than zero, implying the metallic character of MoAlB. In addition, it is noticed that the E_f exactly locates in the valley position of the TDOS, which is a portent of decent stability. By analyzing the PDOS of different atoms, it can be found that the DOS at E_f is mainly contributed to by the d states of Mo or the corresponding metal atoms. In other words, Mo, or the doped transition metal atoms, play the dominant role in the electronic conduction of MoAlB.

Figure 5. The total, and partial, density of states of: (a) $\text{Mo}_4\text{Al}_4\text{B}_4$; (b) $\text{Mo}_4\text{Al}_3\text{SiB}_4$; (c) $\text{Mo}_3\text{CrAl}_4\text{B}_4$; (d) $\text{Mo}_3\text{WAl}_4\text{B}_4$; (e) $\text{Mo}_3\text{NbAl}_4\text{B}_4$.

From Figure 5a, the valence band below -7.0 eV is mainly constituted from the *s* and *p* states of B and Al. The corresponding hybridizations account for the chemical bonding between B-B, Al-B, and probably Al-Al in MoAlB . From -7.0 to -3.0 eV, the highest peak is mainly attributed to the strong hybridizations among B-*s*, Al-*p*, and Mo-*d* orbitals, which renders into the formations of strong covalent bonding of Mo-B and Al-B. Moreover, the considerably high valence bands, with the peak centered around -1.2 eV, are mainly composed of the hybridization between Al-*p* and Mo-*d* states, indicating the

relatively weak Mo-Al bonds. In Si doped MoAlB, the *s* and *p* states of Si make significant contributions to the valence bands below -7.0 eV, as shown in Figure 5b, which is possibly to facilitate the formation of Si-B bonds. In addition, the valence bands from -7.0 to -3.0 eV mainly originate from B-*p*, Al-*p*, Si-*p*, and Mo-*d* states, indicating the formation of covalent bonds between Mo, Al, B, and Si atoms, except for the initial Mo-B and Al-B bonds. Thus, the elastic properties of MoAlB are supposed to be improved due to the enhancement of internal bonding. However, after the doping of transition metal atoms of Cr, W, or Nb, the main differences in the states hybridization can be found to appear from -7.0 eV to *E_f*, originating from the contribution of their *d* states, as shown in Figure 5c to e. Herein, W is found to show the strongest hybridization with Mo, Al, and B, at around -4.0 eV, where the DOS peak is located, as shown in Figure 5d. In this case, the chemical bondings of W with Mo, Al, and B are hypothesized to be consequently intensified. Nevertheless, Cr and Nb mainly participate in the hybridization with Mo and Al at around -1.2 eV, which is deemed to affect the bonds of Mo (Cr or Nb)-Al.

To clearly elucidate the type of chemical bonding as well as the corresponding evolution of the bonding strength with elemental doping, the bond lengths and overlapped populations have been analyzed and listed in Table 5. Simultaneously, the electron density distributions on the (1 0 0) and (1 0 1) crystal planes have been depicted as shown in Figure 6. From Table 5, it can be visibly found that the B-B bond has the shortest bond length and largest population (much larger than 1), indicating the strongest B-B covalent bonding. This conclusion can be confirmed from Figure 6a, in which a significantly high electron density can be observed between B-B atoms. The bonding between B-B shows apparently directional characters. In addition, Al-B and Mo-B bonds have overlapped populations much smaller than one, indicating mixed ionic and covalent bondings. However, the populations of Al-Al and Al-Mo bonds are extremely close to one, implying a significant tendency to covalent bonding. Herein, a negative value of overlapped population appears, basically for the bonds with a long distance. Generally, the negative population implies the antibonding or nonbonding between the two atoms.

Table 5. The calculated bond lengths and overlapped populations (*P* (dimensionless) and *L* (Å) representing the population and bond length, respectively).

Mo ₄ Al ₄ B ₄			Mo ₄ Al ₃ SiB ₄			Mo ₃ CrAl ₄ B ₄		
Bonds	<i>P</i>	<i>L</i> (Å)	Bonds	<i>P</i>	<i>L</i> (Å)	Bonds	<i>P</i>	<i>L</i> (Å)
B-B	1.37	1.81	B-B	1.42	1.80	B-B	1.40	1.80
Al-B	0.16	2.32	Al/Si-B	0.20	2.29	Al-B	0.15	2.30
Mo-B	−0.01	2.35	Mo-B	0.00	2.34	Mo/Cr-B	−0.02	2.31
Mo-B	0.66	2.37	Mo-B	0.57	2.38	Mo/Cr-B	0.66	2.34
Al-Al	0.95	2.67	Al/Si-Al	0.95	2.64	Al-Al	0.97	2.66
Al-Mo	0.73	2.71	Al/Si-Mo	0.81	2.69	Al-Mo/Cr	0.71	2.69
Al-Mo	−0.22	2.99	Al-Mo	−0.23	2.87	Al-Cr	−0.18	2.94
Mo-Mo	−0.96	2.94	Mo-Mo	−0.93	2.97	Mo/Cr-Mo	−0.96	2.90

Mo ₃ WAl ₄ B ₄			Mo ₃ NbAl ₄ B ₄		
Bonds	<i>P</i>	<i>L</i> (Å)	Bonds	<i>P</i>	<i>L</i> (Å)
B	1.33	1.82	B-B	1.39	1.82
Al-B	0.13	2.32	Al-B	0.15	2.36
Mo/W-B	0.00	2.35	Mo/Nb-B	0.00	2.35
Mo/W-B	0.72	2.37	Mo/Nb-B	0.65	2.38
Al-Al	0.92	2.66	Al-Al	0.96	2.68
Al-Mo/W	0.79	2.71	Al-Mo/Nb	0.73	2.74
Al-Mo/W	−0.20	2.98	Al-Mo	−0.22	2.98
Mo-Mo/W	−0.81	2.94	Mo/Nb-Mo	−1.01	2.95

Figure 6. Electron density of the (1 0 0) plane of $\text{Mo}_4\text{Al}_4\text{B}_4$ (a), and the (1 0 1) plane of (b) $\text{Mo}_4\text{Al}_4\text{B}_4$, (c) $\text{Mo}_4\text{Al}_3\text{SiB}_4$, (d) $\text{Mo}_3\text{CrAl}_4\text{B}_4$, (e) $\text{Mo}_3\text{WAl}_4\text{B}_4$, (f) $\text{Mo}_3\text{NbAl}_4\text{B}_4$.

After the introduction of Si, Cr, W, and Nb atoms, the B-B bond changes little, maintaining to show strong B-B covalent bonding, as listed in Table 5. However, it is worth noting that Si addition contributes to intensifying the Al/Si-B and Al/Si-Mo bonds, by increasing the bond population but decreasing the bond length. As shown in Figure 6b and c, it can be visible that the electron densities between Si-B and Si-Mo are much higher compared with the initial MoAlB crystal. Additionally, the bond length of Si-Al is observed to be shortened due to the smaller radius of Si. Consequently, as a sacrifice, the Mo-B bonds adjacent to the doped Si atom seem to be weakened, as shown in Figure 6c, which can also be confirmed from the decreased population. From Figure 6d, it can be found that the Al-Al bonds can be enhanced to some degree, while the other bonds change little after Cr doping. Intriguingly, W-B and W-Al bonds can be apparently intensified with a higher electron density, as displayed in Figure 6e, which is also consistent with the results of bond population in Table 5. Thus, the improvement of the elastic properties of MoAlB after W doping can be explained from the perspective of bonding characters. For $\text{Mo}_3\text{NbAl}_4\text{B}_4$, nearly all bonds can be extended due to the larger atomic radius, so that the bonding strength around Nb can be weakened somewhat. The worst mechanical performances of $\text{Mo}_3\text{NbAl}_4\text{B}_4$ are reasonable from the discussion above.

3.5. Debye Temperature

Debye temperature (θ_D) is an important fundamental parameter in evaluating the physical properties of solids, for instance, the melting temperature, thermal expansion, and specific heat. It can be estimated by the average sound velocity (v_m), according to Equation (20) [49,50,60,61]:

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (20)$$

where k_B , h , and N_A are the Boltzmann, Planck, and Avogadro constants, respectively; n is the number of atoms in each formula; ρ is the density; and M is the molecular weight. Herein, the average sound velocity (v_m) can be calculated by Equation (21) [49,50,60]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (21)$$

where v_t and v_l are the transversal and longitudinal sound velocities, respectively. The v_t and v_l can be obtained by the elastic moduli B and G , according to Navier's equation [49,50,60], as shown below:

$$v_t = \sqrt{\frac{G}{\rho}} \quad (22)$$

$$v_l = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \quad (23)$$

The calculated sound velocities and Debye temperatures (θ_D) of the five calculated crystals have been summarized in Table 6. The Debye temperature of MoAlB is considerably high, indicating its correspondingly good thermal conductivity and strong average chemical bonding. After the introduction of Si, Cr, W, and Mo atoms, V_t and V_l change little, except that the V_l of Mo₃WAl₄B₄ decreases dramatically. Not surprisingly, the average sound velocity shows a remarkable decrease, accounting for the lowest θ_D of Mo₃WAl₄B₄, as shown in Figure 7. In this case, W doping is supposed to weaken the average atomic bonding of MoAlB. By comparison, Si and Cr doping can trigger the increase of θ_D of MoAlB. On the other hand, the melting temperature (T_m) can be empirically obtained with the aid of calculated elastic constants by Equation (24) [62]:

$$T_m = 354 + 1.5(2C_{11} + C_{33}) \quad (24)$$

where C_{11} and C_{33} are the elastic constants in Table 2, respectively. As the structural material applied in the high-temperature fields, the melting point is a fairly important parameter that affects MoAlB's application potential. From Figure 7, it can be visibly found that Mo₄Al₃SiB₄ and Mo₃WAl₄B₄ possess higher T_m than the initial MoAlB. Generally, the melting temperature is tightly associated with the strong covalent bonding in the solid. Thus, the considerable T_m can provide some evidence of the enhancement of covalent bonding after Si and W doping. In conclusion, we can conclude that Si is supposed to be the best doping element to ameliorate the mechanical and physical performance of MoAlB, which will be verified through experimental research in the future.

Table 6. The calculated average, transversal, and longitudinal sound velocities of MoAlB.

Species	V_l (Km/s)	V_t (Km/s)	V_m (Km/s)	θ_D (K)
Mo ₄ Al ₄ B ₄	7.98	4.78	5.29	694.54
Mo ₄ Al ₃ SiB ₄	8.02	4.77	5.28	696.19
Mo ₃ CrAl ₄ B ₄	8.11	4.87	5.39	713.18
Mo ₃ WAl ₄ B ₄	7.45	4.46	4.93	647.12
Mo ₃ NbAl ₄ B ₄	7.92	4.76	5.26	685.81

Figure 7. Debye temperature and melting point.

4. Conclusions

In the present work, the effects of Si, Cr, W, and Nb doping on the phase stability, mechanical properties, chemical bonding, and electronic structures of MoAlB crystal have been investigated by DFT calculations. The main conclusions can be summarized:

1. The initial MoAlB, as well as the element (Si, Cr, W and Nb) doped crystals, are thermodynamically stable, confirmed by the negative cohesive energy and formation enthalpy.
2. MoAlB possesses a considerably high Young's modulus, but it is intrinsically brittle with a B/G ratio less than 1.75. Si and W doping can not only enhance the Young's modulus of MoAlB but also improve its ductility. However, Cr and Nb play a negative role in the elastic moduli as well as the ductility.
3. MoAlB exhibits significant elastic anisotropy: it shows the largest stiffness along the [1 1 1] direction, while it is the most compressible along [0 1 0]. Si and W doping benefit weakening of the anisotropy of Young's modulus by strengthening the Young's moduli along [0 1 0].
4. According to the investigation of DOS, Mulliken populations, and electron density distribution, strong covalent bonding is supposed to exist in MoAlB, combined with ionic and metallic bonding. Si doping significantly intensifies the covalent bondings of Si-B, Si-Mo, and B-B, which accounts for the improved mechanical properties.
5. Si doping can simultaneously increase the Debye temperature and melting point of MoAlB, which apparently shows superior ameliorating effects compared to the other elements. Overall, Si is supposed to be the best dopant in optimizing the comprehensive performance of MoAlB.

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References

1. Türkmen, İ.; Yalamaç, E.; Keddari, M. Investigation of tribological behaviour and diffusion model of Fe₂B layer formed by pack-boriding on SAE 1020 steel. *Surf. Coat. Tech.* **2019**, *377*, 124888. [\[CrossRef\]](#)
2. Iyer, A.K.; Zhang, Y.; Scheifers, J.P.; Fokwa, B.P.T. Structural variations, relationships and properties of M2B metal borides. *J. Solid State Chem.* **2019**, *270*, 618–635. [\[CrossRef\]](#)
3. Fahrenholtz, W.G.; Hilmas, G.E.; Talmy, I.G.; Zaykoski, J.A. Refractory Diborides of Zirconium and Hafnium. *J. Am. Ceram. Soc.* **2007**, *90*, 1347–1364. [\[CrossRef\]](#)
4. Jeitschko, W. Die Kristallstruktur von MoAlB. *Mon. Chem.* **1966**, *97*, 1472–1476. [\[CrossRef\]](#)
5. Kota, S.; Zapata-Solvas, E.; Ly, A.; Lu, J.; Elkassabany, O.; Huon, A.; Lee, W.E.; Hultman, L.; May, S.J.; Barsoum, M.W. Synthesis and Characterization of an Alumina Forming Nanolaminated Boride: MoAlB. *Sci. Rep.* **2016**, *6*, 26475. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Barsoum, M.W. The M_{N+1}AX_N phases: A new class of solids: Thermodynamically stable nanolaminates. *Prog. Solid State Chem.* **2000**, *28*, 201–281. [\[CrossRef\]](#)
7. Radovic, M.; Barsoum, M.W. MAX phases: Bridging the gap between metals and ceramics. *Am. Ceram. Soc. Bull.* **2013**, *92*, 20–27.
8. Wang, X.H.; Zhou, Y.C. Layered Machinable and Electrically Conductive Ti₂AlC and Ti₃AlC₂ Ceramics: A Review. *J. Mater. Sci. Technol.* **2010**, *26*, 385–416. [\[CrossRef\]](#)
9. Eklund, P.; Beckers, M.; Jansson, U.; Högberg, H.; Hultman, L. The M_{n+1}AX_n phases: Materials science and thin-film processing. *Thin Solid Films.* **2010**, *518*, 1851–1878. [\[CrossRef\]](#)
10. Wang, X.; Zhang, H.; Zheng, L.; Ma, Y.; Lu, X.; Sun, Y.; Zhou, Y. Ti₅Al₂C₃: A New Ternary Carbide Belonging to MAX Phases in the Ti–Al–C System. *J. Am. Ceram. Soc.* **2012**, *95*, 1508–1510. [\[CrossRef\]](#)
11. Ade, M.; Hillebrecht, H. Ternary Borides Cr₂AlB₂, Cr₃AlB₄, and Cr₄AlB₆: The First Members of the Series (CrB₂)_nCrAl with n = 1, 2, 3 and a Unifying Concept for Ternary Borides as MAB-Phases. *Inorg. Chem.* **2015**, *54*, 6122–6135. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Kota, S.; Zapata-Solvas, E.; Chen, Y.; Radovic, M.; Lee, W.E.; Barsoum, M.W. Isothermal and Cyclic Oxidation of MoAlB in Air from 1100 °C to 1400 °C. *J. Electrochem. Soc.* **2017**, *164*, 930–938. [\[CrossRef\]](#)
13. Lou, T. Microstructure and Properties of Spark Plasma Sintered MoAlB Ceramics. Master's Thesis, University of Nebraska-Lincoln, Lincoln, NE, USA, 2016.
14. Xu, L.; Shi, O.; Liu, C.; Zhu, D.; Grasso, S.; Hu, C. Synthesis, microstructure and properties of MoAlB ceramics. *Ceram. Int.* **2018**, *44*, 13396–13401. [\[CrossRef\]](#)
15. Bei, G.; van der Zwaag, S.; Kota, S.; Barsoum, M.W.; Sloof, W.G. Ultra-high temperature ablation behavior of MoAlB ceramics under an oxyacetylene flame. *J. Eur. Ceram. Soc.* **2019**, *39*, 2010–2017. [\[CrossRef\]](#)
16. Benamor, A.; Kota, S.; Chiker, N.; Haddad, A.; Hadji, Y.; Natsu, V.; Abdi, S.; Yahi, M.; Benamar, M.E.; Sahraoui, T.; et al. Friction and wear properties of MoAlB against Al₂O₃ and 100Cr6 steel counterparts. *J. Eur. Ceram. Soc.* **2019**, *39*, 868–877. [\[CrossRef\]](#)
17. Chen, Y.; Kota, S.; Barsoum, M.W.; Radovic, M. Compressive deformation of MoAlB up to 1100 °C. *J. Alloy. Compd.* **2019**, *774*, 1216–1222. [\[CrossRef\]](#)
18. Kota, S.; Sokol, M.; Barsoum, M.W. A progress report on the MAB phases: Atomically laminated, ternary transition metal borides. *Int. Mater. Rev.* **2020**, *65*, 226–255. [\[CrossRef\]](#)
19. Lu, X.; Li, S.; Zhang, W.; Yao, B.; Yu, W.; Zhou, Y. Crack healing behavior of a MAB phase: MoAlB. *J. Eur. Ceram. Soc.* **2019**, *39*, 4023–4028. [\[CrossRef\]](#)
20. Lu, X.; Li, S.; Zhang, W.; Yu, W.; Zhou, Y. Thermal shock behavior of a nanolaminated ternary boride: MoAlB. *Ceram. Int.* **2019**, *45*, 9386–9389. [\[CrossRef\]](#)
21. Shi, O.; Xu, L.; Jiang, A.; Xu, Q.; Xiao, Y.; Zhu, D.; Grasso, S.; Hu, C. Synthesis and oxidation resistance of MoAlB single crystals. *Ceram. Int.* **2019**, *45*, 2446–2450. [\[CrossRef\]](#)
22. Wang, S.; Xu, Y.; Yu, Z.; Tan, H.; Du, S.; Zhang, Y.; Yang, J.; Liu, W. Synthesis, microstructure and mechanical properties of a MoAlB ceramic prepared by spark plasma sintering from elemental powders. *Ceram. Int.* **2019**, *45*, 23515–23521. [\[CrossRef\]](#)
23. Su, X.; Dong, J.; Chu, L.; Sun, H.; Grasso, S.; Hu, C. Synthesis, microstructure and properties of MoAlB ceramics prepared by in situ reactive spark plasma sintering. *Ceram. Int.* **2020**, *46*, 15214–15221. [\[CrossRef\]](#)
24. Yu, Z.; Tan, H.; Wang, S.; Cheng, J.; Sun, Q.; Yang, J.; Liu, W. High-temperature tribological behaviors of MoAlB ceramics sliding against Al₂O₃ and Inconel 718 alloy. *Ceram. Int.* **2020**, *46*, 14713–14720. [\[CrossRef\]](#)

25. Wei, X.; Chen, Z.; Zhong, J.; Wang, L.; Yang, W.; Wang, Y. Effect of alloying elements on mechanical, electronic and magnetic properties of Fe₂B by first-principles investigations. *Comp. Mater. Sci.* **2018**, *147*, 322–330.
26. Rojacz, H.; Premauer, M.; Varga, M. Alloying and strain hardening effects in abrasive contacts on iron based alloys. *Wear* **2018**, *410*, 173–180. [[CrossRef](#)]
27. Park, N.; Lee, S.-C.; Cha, P.-R. Effects of alloying elements on the stability and mechanical properties of Fe₃Al from first-principles calculations. *Comp. Mater. Sci.* **2018**, *146*, 303–309. [[CrossRef](#)]
28. Wang, C.; Yan, L.; Han, J.; Xu, W.; Deng, B.; Liu, X. Effects of alloying elements on the structural, elastic and thermodynamic properties of Co₃Ta compounds from first-principles calculations. *J. Alloy. Compd.* **2017**, *726*, 490–497. [[CrossRef](#)]
29. Jian, Y.; Huang, Z.; Xing, J.; Gao, Y. Effects of chromium on the morphology and mechanical properties of Fe₂B intermetallic in Fe-3.0B alloy. *J. Mater. Sci.* **2018**, *53*, 5329–5338. [[CrossRef](#)]
30. Jian, Y.; Huang, Z.; Liu, X.; Sun, J.; Xing, J. Microstructure, mechanical properties and toughening mechanism of directional Fe₂B crystal in Fe-B alloy with trace Cr addition. *J. Mater. Sci. Technol.* **2020**, *57*, 172–179. [[CrossRef](#)]
31. Jian, Y.; Huang, Z.; Xing, J.; Guo, X.; Wang, Y.; Lv, Z. Effects of Mn addition on the two-body abrasive wear behavior of Fe-3.0 wt% B alloy. *Tribol. Int.* **2016**, *103*, 243–251. [[CrossRef](#)]
32. Shen, Y.; Huang, Z.; Xiao, P.; Zhang, L.; Li, K.; Cao, Z.; Jian, Y. Sintering mechanism, microstructure evolution and nanomechanical properties of Cr-added Mo₂FeB₂ based cermets. *Ceram. Int.* **2020**, *46*, 15482–15491. [[CrossRef](#)]
33. Okada, S.; Iizumi, K.; Kudaka, K.; Kudou, K.; Miyamoto, M.; Yu, Y.; Lundström, T. Single Crystal Growth of (Mo_xCr_{1-x})AlB and (Mo_xW_{1-x})AlB by Metal Al Solutions and Properties of the Crystals. *J. Solid State Chem.* **1997**, *133*, 36–43. [[CrossRef](#)]
34. Ma, P.; Li, S.; Hu, J.; Lu, X.; Yu, W.; Zhou, Y. Processing and characterization of MoAl_{1-x}Si_xB solid solutions. *J. Alloy. Compd.* **2020**, *814*, 152290. [[CrossRef](#)]
35. Li, X.; Cui, H.; Zhang, R. First-principles study of the electronic and optical properties of a new metallic MoAlB. *Sci. Rep.* **2016**, *6*, 39790. [[CrossRef](#)]
36. Bai, Y.; Qi, X.; Duff, A.; Li, N.; Kong, F.; He, X.; Wang, R.; Lee, W.E. Density functional theory insights into ternary layered boride MoAlB. *Acta Mater.* **2017**, *132*, 69–81. [[CrossRef](#)]
37. Xiang, H.; Feng, Z.; Li, Z.; Zhou, Y. Theoretical investigations on mechanical and dynamical properties of MAlB (M = Mo, W) nanolaminated borides at ground-states and elevated temperatures. *J. Alloy. Compd.* **2018**, *738*, 461–472. [[CrossRef](#)]
38. Ali, M.M.; Hadi, M.A.; Rahman, M.L.; Haque, F.H.; Haider, A.F.M.Y.; Aftabuzzaman, M. DFT investigations into the physical properties of a MAB phase Cr₄AlB₄. *J. Alloy. Compd.* **2020**, *821*, 153547. [[CrossRef](#)]
39. Payne, M.C.; Teter, M.P.; Allan, D.C.; Arias, T.A.; Joannopoulos, A.J. Iterative minimization techniques for ab initio total-energy calculations: Molecular dynamics and conjugate gradients. *Rev. Mod. Phys.* **1992**, *64*, 1045–1097. [[CrossRef](#)]
40. Segall, M.D.; Lindan, P.J.; Probert, M.A.; Pickard, C.J.; Hasnip, P.J.; Clark, S.J.; Payne, M.C. First-principles simulation: Ideas, illustrations and the CASTEP code. *J. Phys. Condens. Matter.* **2002**, *14*, 2717–2744. [[CrossRef](#)]
41. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [[CrossRef](#)]
42. Hammer, B.; Hansen, L.B.; Nørskov, J.K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421. [[CrossRef](#)]
43. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895. [[CrossRef](#)] [[PubMed](#)]
44. Pfrommer, B.G.; Côté, M.; Louie, S.G.; Cohen, M.L. Relaxation of Crystals with the Quasi-Newton Method. *J. Comput. Phys.* **1997**, *131*, 233–240. [[CrossRef](#)]
45. Zhang, P.; Zhou, Y.; Yang, J.; Li, D.; Ren, X.; Yang, Y.; Yang, Q. Optimization on mechanical properties of Fe_{7-x}Cr_xC₃ carbides by first-principles investigation. *J. Alloy. Compd.* **2013**, *560*, 49–53. [[CrossRef](#)]
46. Lu, J.; Kota, S.; Barsoum, M.W.; Hultman, L. Atomic structure and lattice defects in nanolaminated ternary transition metal borides. *Mater. Res. Lett.* **2016**, *5*, 235–241. [[CrossRef](#)]

47. Dai, F.-Z.; Feng, Z.; Zhou, Y. First-principles investigation on the chemical bonding, elastic properties and ideal strengths of MoAlB and WAlB nanolaminated MAB phases. *Comp. Mater. Sci.* **2018**, *147*, 331–337. [\[CrossRef\]](#)
48. Feng, J.; Xiao, B.; Chen, J.; Du, Y.; Yu, J.; Zhou, R. Stability, thermal and mechanical properties of Pt_xAl_y compounds. *Mater. Design.* **2011**, *32*, 3231–3239. [\[CrossRef\]](#)
49. Wu, J.; Chong, X.; Jiang, Y.; Feng, J. Stability, electronic structure, mechanical and thermodynamic properties of Fe-Si binary compounds. *J. Alloy. Compds.* **2017**, *693*, 859–870. [\[CrossRef\]](#)
50. Jian, Y.; Huang, Z.; Xing, J.; Sun, L.; Liu, Y.; Gao, P. Phase stability, mechanical properties and electronic structures of Ti Al binary compounds by first principles calculations. *Mater. Chem. Phys.* **2019**, *221*, 311–321. [\[CrossRef\]](#)
51. Jian, Y.; Huang, Z.; Liu, X.; Xing, J. Comparative investigation on the stability, electronic structures and mechanical properties of Mo_2FeB_2 and Mo_2NiB_2 ternary borides by first-principles calculations. *Results Phys.* **2019**, *15*, 102698. [\[CrossRef\]](#)
52. Patil, S.; Khare, S.; Tuttle, B.; Bording, J.; Kodambaka, S. Mechanical stability of possible structures of PtN investigated using first-principles calculations. *Phys. Rev. B* **2006**, *73*, 104118. [\[CrossRef\]](#)
53. Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; The Clarendon Press: Oxford, UK, 1954.
54. Zhou, Y.; Xiang, H.; Zhang, H.; Dai, F.-Z. Theoretical prediction on the stability, electronic structure, room and elevated temperature properties of a new MAB phase Mo_2AlB_2 . *J. Mater. Sci. Technol.* **2019**, *35*, 2926–2934. [\[CrossRef\]](#)
55. Chung, D.; Buessem, W. The Voigt-Reuss-Hill Approximation and Elastic Moduli of Polycrystalline MgO, CaF_2 , β -ZnS, ZnSe, and CdTe. *J. Appl. Phys.* **1967**, *38*, 2535–2540. [\[CrossRef\]](#)
56. Kota, S.; Agne, M.; Zapata-Solvas, E.; Dezellus, O.; Lopez, D.; Gardiola, B.; Radovic, M.; Barsoum, M.W. Elastic properties, thermal stability, and thermodynamic parameters of MoAlB. *Phys. Rev. B* **2017**, *95*. [\[CrossRef\]](#)
57. Pugh, S.F. XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Lond. Edinb. Dubl. Phil. Mag. J. Sci.* **1954**, *45*, 823–843. [\[CrossRef\]](#)
58. He, L.; Lin, Z.; Wang, J.; Bao, Y.; Li, M.; Zhou, Y. Synthesis and Characterization of Bulk $Zr_2Al_3C_4$ Ceramic. *J. Am. Ceram. Soc.* **2007**, *90*, 3687–3689. [\[CrossRef\]](#)
59. Bai, Y.; Duff, A.; Jayaseelan, D.D.; Wang, R.; He, X.; Lee, W.E. DFT Predictions of Crystal Structure, Electronic Structure, Compressibility, and Elastic Properties of Hf–Al–C Carbides. *J. Am. Ceram. Soc.* **2016**, *99*, 3449–3457. [\[CrossRef\]](#)
60. Sun, Z.; Li, S.; Ahuja, R.; Schneider, J.M. Calculated elastic properties of M_2AlC ($M = Ti, V, Cr, Nb$ and Ta). *Solid State Commun.* **2004**, *129*, 589–592. [\[CrossRef\]](#)
61. Feng, J.; Xiao, B.; Zhou, R.; Pan, W.; Clarke, D.R. Anisotropic elastic and thermal properties of the double perovskite slab–rock salt layer $Ln_2SrAl_2O_7$ ($Ln = La, Nd, Sm, Eu, Gd$ or Dy) natural superlattice structure. *Acta Mater.* **2012**, *60*, 3380–3392. [\[CrossRef\]](#)
62. Chen, H.; Yang, L.; Long, J. First-principles investigation of the elastic, Vickers hardness and thermodynamic properties of Al–Cu intermetallic compounds. *Superlattices Microst.* **2015**, *79*, 156–165. [\[CrossRef\]](#)