Structural Stability, Electronic Structures, Mechanical Properties and Debye Temperature of Transition Metal Impurities in Tungsten: A First-Principles Study

Diyou Jiang 1, Musheng Wu 2, Desheng Liu 3, Fangfang Li 1, Minggang Chai 1 and Sanqiu Liu 4,*

1 Key Laboratory of Nondestructive Testing, Ministry of Education, Nanchang Hangkong University, Nanchang 330063, China
2 Department of Physics, Jiangxi Normal University, Nanchang 330022, China
3 School of Energy and Machinery engineering, Jiangxi University of Science and Technology, Nanchang 330013, China
4 Department of Physics, Nanchang University, Nanchang 330047, China
* Correspondence: sjlgroup@ncu.edu.cn; Tel.: +86-0791-83969511

Received: 20 July 2019; Accepted: 27 August 2019; Published: 2 September 2019

Abstract: The structural stability, electronic structures, mechanical properties and Debye temperature of W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys have been investigated by first principles method. The lattice constant, cell volume, formation energy and cohesive energy of W-TM alloys are calculated. W-TM alloys still maintain bcc lattice, and have no structural phase transformation. It is shown that W-Mo and W-Mn alloys have better alloying ability with strong interactions between W and Mo/Mn atoms. However, the alloying ability of W-Cu, W-Fe, W-Cr and W-Ni is poor, and there is a weak chemical interaction between W and Cu/Cr/Fe/Ni atoms. Using the optimized lattice, the elastic constants are calculated, and the elastic moduli and other mechanical parameters are derived. Results show that the mechanical strength of W-TM alloys is lower than that of pure W, especially W-Cu and W-Ni alloys. However, the B/G ratio and Poisson’s ratio of W-TM alloys are higher than that of pure W, indicating that TM alloying can significantly improve the ductility of pure W. The metallicity of pure W can be enhanced by doping Fe or Mn, while doping Cr, Cu, Mo and Ni reduces the metallicity of pure W, of which W-Cu alloy has worst metallicity.

Keywords: W alloys; phase stability; mechanical properties; melting point and hardness; Debye temperature; the first principles

1. Introduction

Pure tungsten (W) as a metallic material has some attractive engineering properties, including high melting temperature (about 3683 K), high strength at high temperatures, good thermal conductivity, low thermal expansion coefficient, high sputtering threshold energy and low sputtering erosion [1–3]. Therefore, it is very important for practical applications where components are exposed to high temperatures. Recently, in the International Thermonuclear Experimental Reactor (ITER), pure W is receiving attention as a most promising candidate material for plasma facing materials (PFMs), and it is of interest as a divertor plates in fusion power reactors. At the same time, tungsten is also thought as a shielding material in fusion power reactors and other systems involving nuclear fusion reactions [4]. However, pure tungsten has the problems of poor radiation stability, fracture toughness and low-temperature brittleness, low ductility associated with a high ductile-to-brittle transition.
temperature (DBTT). Alloynng is a good method to improve the engineering properties of pure tungsten metal. As an example, the thermodynamic properties of pure tungsten metal can be improved by alloying with other elements [5–7]. The transition metal (TM) elements are selected as substitution solutes. Some of them are incorporated into W to improve its properties. For example, it has been suggested to add elements such as Re, Ta, Ti, Mo, V, Hf and Zr to W in order to improve the ductility of pure tungsten metal [8–14]. However, it is worth noting that there are a small amount of transition metal impurities in tungsten, such as Cr, Cu, Fe, Mn, Mo and Ni [15,16]. These TM impurities must have an effect on the properties of pure W metal. To date, however, little research has been done on the effects of these TM element impurities on the basic mechanical properties of tungsten metal, such as melting point and hardness, elastic properties and ductile/brittle behaviors. It is well known that the mechanical properties of tungsten materials are very important for PFMs. Debye temperature ($\Theta_D$) is another important physical quantity reflecting the binding force between atoms. Different materials have different Debye temperatures. The larger the $\Theta_D$ is, the stronger the covalent bonding is [17,18]. Therefore, it is necessary to study the Debye temperature of materials. At the same time, the extent to which these TM elements have an effect on the properties of pure tungsten has not been compared. Besides, the density-functional theory (DFT) can be used to predict the engineering properties of materials. Comparing with the experimental evaluation, the theoretical calculation has lower cost and higher efficiency. The reason is that traditional experimental design material methods are expensive and time-consuming. DFT calculations can be used to study the relationship between structure and performance of materials, and provide a basis for material design. Computer simulations focus on improving the specific properties of materials and it can reduce the amount of compositions that needed to be prepared and characterized. Density functional theory (DFT) as an effective approximation method is used to solve the structure of multi-electronic systems [16,19–24], and it obtains the total energy of multi-electronic systems based on the energy minimization method.

In this paper, we thus investigated the Phase stability, electronic structures, mechanical properties and Debye temperature of TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) impurities in tungsten based on first principles method. The lattice constant (LC), cell volume (V), formation energy ($E_f$), cohesive energy ($E_{coh}$), melting point and hardness, elastic constant and Debye temperature of the W-TM alloys are calculated. The ductile/brittle properties of the W-TM alloys are evaluated based on the mechanical characteristic of $B/G$ ratio, Poisson’s ratio ($\nu$) and Cauchy pressure ($C'$). The thermodynamic properties of the W-TM alloys can be understood by calculating the Debye temperature. Besides, the metallicity and anisotropy of the W-TM alloys is also estimated. These calculations provide an effective guide for further optimizing the composition of the W-TM alloys, which can provide a useful database for PFMs research.

2. Model and Computational Details

All models are described by a $3 \times 3 \times 3$ supercell containing 54 atoms in a body centered cubic (bcc) structures. A tungsten atom is substituted by chromium, copper, iron, manganese, molybdenum and nickel atoms in turn, and various alloys with the same concentration are obtained. These supercell structures are pure $W_{54}$, $W_{53}Cr_1$, $W_{53}Cu_1$, $W_{53}Fe_1$, $W_{53}Mn_1$, $W_{53}Mo_1$ and $W_{53}Ni_1$, respectively. Computations in the current work are done with the first principles method based on the pseudo-potential plane-wave within the DFT using Vienna Ab-initio Simulation Package (VASP) [25,26] code. The interaction between core ion and valence electron is described according to the projector augmented wave method (PAW) [27]. The exchange-correlation potentials are described with the generalized gradient approximation (GGA) by Perdew and Wang (PW91) [28]. All the systems are modeled with bcc supercell. For the Brillouin-zone sampling, the k-point is $7 \times 7 \times 7$ Monkhorst-Pack mesh [29] for the W-TM alloys. The cutoff energy of 400 eV is set for all systems. At the same time, both the K point and cutoff energy are tested respectively, which can fully meet the calculation requirements. Spin polarization is considered throughout the calculation. The convergence accuracy of
total energy and interatomic forces is $10^{-5}$ eV and $10^{-3}$ eV/Å, respectively. Gaussian smearing method is applied in all calculations, and the smearing width is 0.05 eV.

Using the continuous elastic theory [30,31], there are three independent elastic constants for cubic crystal system. The elastic constants are $C_{11}$, $C_{12}$ and $C_{44}$, respectively. The elastic constant matrix of cubic crystal as follows:

$$[C] = \begin{bmatrix}
C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & C_{44}
\end{bmatrix}$$

A small strain ($\delta$) is applied to the solid lattice of the W-TM alloys to construct a quadratic function relationship between the total energy changes ($\Delta E$) and the strains ($\delta$) according to the Hooks law, as follows:

$$\Delta E = \frac{V}{2} \sum_{i,j=1}^{6} C_{ij} \varepsilon_i \varepsilon_j$$

where $\Delta E$ is the total energy changes, $V$ is the original unit cell volume, $C_{ij}$ are the elastic constants, $\varepsilon_i$ and $\varepsilon_j$ are the components of strain matrix.

In order to investigate these elastic constants, three sets of specific strains ($\delta$) are applied to the cubic supercell in different directions. As shown in Table 1. The elastic constants can be obtained by fitting the relationship between the total energy changes ($\Delta E$) and the applied strains ($\delta$). Besides, the correlation coefficients between fitting curves and calculation points are all above 0.99, which shows that the calculation accuracy and method can ensure more accurate mechanical constants.

**Table 1.** The relationship between the strains ($\delta$) and the total energy changes ($\Delta E$) of cubic crystal system.

| Strain | Change of Total Energy |
|--------|------------------------|
| $e = (0,0,0,\delta,\delta)$ | $\Delta E = \frac{3}{2} C_{44} \delta^2$ |
| $e = (\delta,\delta,0,0,0)$ | $\Delta E = (C_{11} + C_{12}) \delta^2$ |
| $e = (\delta,\delta,0,0,0)$ | $\Delta E = \frac{2}{3} (C_{11} + 2C_{12}) \delta^2$ |

The mechanical parameters of the W-TM alloys can be calculated by using single crystal elastic constants according to the Voigt-Reuss-Hill scheme [32–35]. The bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), Poisson’s ratio ($\nu$), Cauchy pressure ($C'$) and anisotropy coefficients ($A$) of the W-TM alloys are calculated by using $C_{11}$, $C_{12}$ and $C_{44}$, as follows:

$$B = \frac{C_{11} + 2C_{12}}{3},$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5},$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})},$$

$$G = \frac{G_V + G_R}{2},$$

$$E = \frac{9BG}{3B + G},$$

$$\nu = \frac{3B - 2G}{2(3B + G)}.$$
In order to research the thermodynamic properties of the W-TM alloys, the Debye temperature ($\Theta_D$) of these materials is calculated. The Debye temperature can be calculated from elastic constants by taking the average sound velocity ($v_m$), as follows [36]:

$$\Theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{m} \right) \right]^{\frac{1}{3}} v_m$$

(10)

where $h$ is the Planck’s constant, $k_B$ is the Boltzmann’s constant, $n$ is the total number of atoms per formula, $N_A$ is the Avogadro number, $\rho$ is the mass density, $m$ is the molecular weight.

The average wave velocity ($v_m$) of the W-TM alloy materials can be approximately calculated by using the following Equation [36]:

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

(11)

where $v_s$ and $v_l$ are the shear and longitudinal sound velocities of the W-TM alloys, respectively, which can be obtained by taking the values of Hill’s B and G based on the approach of Voigt-Reuss-Hill according to the following Equations [37]:

$$v_s = \left( \frac{G}{\rho} \right)^{\frac{1}{2}}$$

(12)

$$v_l = \left( \frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}}$$

(13)

3. Results and Discussion

3.1. Crystal Configurations and Lattice Constants

Firstly, the atomic positions and crystal configurations of the W-TM alloys in the supercell are considered and optimized, and these optimized atomic configurations (a local minimum) are chosen for further study. As it is shown in Figure 1, the W-TM alloys still keep the bcc lattice, and the TM atoms are located at a certain position to ensure high symmetry of these configurations. This result indicates that the W-TM alloys can be formed at the atomic level.
In order to investigate the equilibrium lattice constants of the W-TM alloys, the total energy as a function of the volume is calculated and then using Birch-Murnaghan equation of state to fit these results. Figure 2 shows the equilibrium lattice constants of the W-TM alloys with doping different TM impurities. The present calculation results show that the equilibrium lattice constant of bcc tungsten is 3.176 Å, which is in good agreement with other theoretical and experimental data [38–41]. It indicates that our calculation results are accurate. The lattice constants of the W-TM alloys are lower than that of pure W, due to the smaller radius of the TM atoms comparing with that of W atom. Of note, however, the lattice constants of the W-Cu and W-Ni alloys are anomalous comparing with those of other alloys. It is known that the atomic radii of W, Cr, Cu, Fe, Mn, Mo and Ni are 2.02 Å, 1.85 Å, 1.57 Å, 1.72 Å, 1.79 Å, 2.01 Å and 1.62 Å, respectively. Normally, the lattice constant of the W-Cu alloy is the smallest, yet it is higher than that of the W-Ni alloy, and even higher than that of the W-Cr, W-Fe and W-Mn alloys.

Figure 2. Equilibrium lattice constants (a) and formation energies (b) of pure W and the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys.

It can be seen from Table 2 that the lattice constant of the W-Ni alloy is also higher than that of the W-Cr, W-Fe and W-Mn alloys. This abnormal lattice constant expansion indicates that the alloying ability of the two materials is poor.

3.2. Formation and Cohesive Energies

In order to evaluate the structural stability of the W-TM alloys, the formation energy \( E_f \) and cohesive energy \( E_{coh} \) of the W-TM alloys with an anti-site are calculated according to the following equation:

\[
E_f = \frac{1}{m + n} \left[ E^{AB}_{\text{total}} - mE^A_{\text{solid}} - nE^B_{\text{solid}} \right]
\]  

\( (14) \)
\[
E_{\text{coh}} = \frac{1}{m+n} \left[ E_{\text{total}}^{AB} - mE_{\text{atom}}^A - nE_{\text{atom}}^B \right] \tag{15}
\]

where \( m \) and \( n \) refer to the numbers of W and TM atoms, respectively. \( E_{\text{solid}}^A \) and \( E_{\text{solid}}^B \) is the average energy of per atom with pure W and TM in the solid states, respectively. \( E_{\text{atom}}^A \) and \( E_{\text{atom}}^B \) is the energy of W and TM free atoms in the cell lattice, respectively. \( E_{\text{total}}^{AB} \) is the total energy of the W-TM alloys with an anti-site in the bcc lattice.

Using Equations (14) and (15), the formation energy and cohesive energy for the six alloys have been calculated via the total energies based on our DFT calculations. The calculated the formation energies and cohesive energies of the W-TM alloys with an anti-site are displayed in Table 2. Simultaneously, in Figure 2, we plotted the formation energies of the W-TM alloys with an anti-site. According to the definition of formation energy, negative formation energy indicates that the alloying ability of the compound is stronger. Meanwhile, the greater absolute value of the cohesive energy is, the more stable structure of the alloy compound is \([42]\). The calculated cohesive energy of pure tungsten is consistent with other theoretical value \([24]\). At the same time, the calculated cohesive energies of chromium, copper, iron, manganese, molybdenum and nickel are 4.12, 3.58, 5.37, 3.17, 6.52 and 5.01 eV/atom, respectively. In the literature, the cohesive energies of chromium, copper, iron, manganese, molybdenum and nickel are 4.02(4.10), 3.49, 5.28(4.28), 2.92, 6.38 and 4.84 eV/atom, respectively \([24, 43]\). It means that the results of the two are consistent. We can see that the W-Mn and W-Mo alloys have the negative formation energy, so it shows that the two alloys have better alloying ability in the W-TM alloys. Meanwhile, the W-Mo alloy has the largest absolute value of cohesive energy, which indirectly reflects that it has the most stable structure in the W-TM alloys. It is worth noting that the W-Mn and W-Mo alloys have negative formation energy, which confirming that there is a strong chemical interaction between W and Mn/Mo atoms. However, the W-Cr, W-Cu, W-Fe and W-Ni alloys exhibit positive formation energies, indicating that there is a weak chemical interaction between W and Cr/Cu/Fe/Ni, and the alloying ability of the four alloys is poor. In particular, the formation energy of the W-Cu alloy is the highest, indicating that its alloying ability is the worst, which is in good agreement with the previous analysis of lattice constants. Of note, the negative formation energy indicates that the material synthesis process is exothermic, and the material is easy to be formed. Conversely, for the endothermic reaction, the material is more difficult to form.

### 3.3. Charge Density

The essence of charge transfer between W and TM is to reduce the energy of the W-TM alloys. It is well known that the electronegativity of W is lower than that of transition elements Cu, Fe and Ni, yet higher than that of Cr, Mn and Mo. Therefore, it is expected that small charge transfer from Cr/Mn/Mo to W and W to Cu/Fe/Ni in these alloys. Figure 3 clearly shows the differential charge density of charge transfer. We can see that tungsten obtains charge in Figure 3a,d,e, and loses charge in Figure 3b,c,f.

Charge transfer can also be analyzed by using the Bader charge analysis. Our results show that the Bader charges of Cr, Cu, Fe, Mn, Mo and Ni are about 5.71e, 11.15e, 8.13e, 6.99e, 5.88e and 10.24e, respectively. As we all know that the valence electrons of Cr, Cu, Fe, Mn, Mo and Ni are 6e, 11e, 8e, 7e, 6e and 10e, respectively. It can be seen that Cr, Mn and Mo lost about 0.285e, 0.013e and 0.121e, respectively, while Cu, Fe and Ni obtained about 0.154e, 0.126e and 0.242e, respectively. The charge transfer produces slightly positively charged Cr/Mn/Mo and negatively charged Cu/Fe/Ni. The major interaction between W and TM atoms is metallic bonding. Although the charge transfer is small, the charge transfer strengthens the metallic bonding of the W-TM alloys. This will be explained in Section 3.4, which discusses the Cauchy pressure.
The elastic constants are usually used to characterize the ability of a material to resist deformation from external forces [44]. It plays an important role in understanding the structural stability and anisotropic behavior of materials. Firstly, the elastic constants of pure W metal are calculated. The results are summarized in Table 2, as well as the previous experimental and theoretical values [40,41,45,46]. It is clear that the results are consistent with other experimental and theoretical values, which indicates that the setting of calculation parameters and the results are credible. Then, the elastic constants of the W-TM alloys are calculated, as shown in Table 2 and plotted in Figure 4. It is well known that the mechanical stability criterion of elastic constants in cubic structure is \[ (C_{11} - C_{12}) > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad (C_{11} + 2C_{12}) > 0. \]

Obviously, the elastic constants of the W-TM alloys satisfy these stability criteria, demonstrating that the structures of the W-TM alloys are mechanically stable. It can be seen from Figure 4 that the elastic constant \( C_{11} \) of the W-TM alloy is lower than that of pure W metal. Among them, the W-Cu alloy has the worst performance, followed by the W-Ni alloy, and the best performance is the W-Mo alloy. The order of the elastic constant \( C_{11} \) from strength to weakness is the W-Mo, W-Cr, W-Mn, W-Fe, W-Ni and W-Cu alloy. The elastic constant \( C_{12} \) of the W-TM alloy has different degrees of increases or decreases comparing with that of pure W metal, yet the amount of increase or decrease is small, and the gap is about 1–2 GPa. The order from strength to weakness is the W-Fe, W-Ni, W-Cu, W-Mn, W-Cr and W-Mo alloy. The elastic constant \( C_{44} \) of the W-TM alloy is also lower than that of pure W metal. However, the decrease is small, about 3–4 GPa. The order from strength to weakness is the W-Mn, W-Ni, W-Fe, W-Cu, W-Mo and W-Cr alloy. To sum up, the impurity elements Cr, Cu, Fe, Mn, Mo and Ni have a greater influence on the elastic constant \( C_{11} \), yet a smaller influence on \( C_{12} \) and \( C_{44} \). The results show that the mechanical strength of the W-TM alloys is lower than that pure W metal, especially the W-Cu and W-Ni alloys.

Figure 3. Charge transfer of the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys. The color and size of W and TM impurities atoms are the same as in Figure 1. The yellow and blue color charge density contours indicate gain and loss charge, respectively. The value of all the isosurface levels is 0.00279115 e/Å³.

3.4. Mechanical Properties

The elastic constants are usually used to characterize the ability of a material to resist deformation from external forces [44]. It plays an important role in understanding the structural stability and anisotropic behavior of materials. Firstly, the elastic constants of pure W metal are calculated. The results are summarized in Table 2, as well as the previous experimental and theoretical values [40,41,45,46]. It is clear that the results are consistent with other experimental and theoretical values, which indicates that the setting of calculation parameters and the results are credible. Then, the elastic constants of the W-TM alloys are calculated, as shown in Table 2 and plotted in Figure 4. It is well known that the mechanical stability criterion of elastic constants in cubic structure is \[ (C_{11} - C_{12}) > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad (C_{11} + 2C_{12}) > 0. \]

Obviously, the elastic constants of the W-TM alloys satisfy these stability criteria, demonstrating that the structures of the W-TM alloys are mechanically stable. It can be seen from Figure 4 that the elastic constant \( C_{11} \) of the W-TM alloy is lower than that of pure W metal. Among them, the W-Cu alloy has the worst performance, followed by the W-Ni alloy, and the best performance is the W-Mo alloy. The order of the elastic constant \( C_{11} \) from strength to weakness is the W-Mo, W-Cr, W-Mn, W-Fe, W-Ni and W-Cu alloy. The elastic constant \( C_{12} \) of the W-TM alloy has different degrees of increases or decreases comparing with that of pure W metal, yet the amount of increase or decrease is small, and the gap is about 1–2 GPa. The order from strength to weakness is the W-Fe, W-Ni, W-Cu, W-Mn, W-Cr and W-Mo alloy. The elastic constant \( C_{44} \) of the W-TM alloy is also lower than that of pure W metal. However, the decrease is small, about 3–4 GPa. The order from strength to weakness is the W-Mn, W-Ni, W-Fe, W-Cu, W-Mo and W-Cr alloy. To sum up, the impurity elements Cr, Cu, Fe, Mn, Mo and Ni have a greater influence on the elastic constant \( C_{11} \), yet a smaller influence on \( C_{12} \) and \( C_{44} \). The results show that the mechanical strength of the W-TM alloys is lower than that pure W metal, especially the W-Cu and W-Ni alloys.
polycrystalline material are deduced from single-crystal elastic constants by using Voigt-Reuss-Hill approximations \[32–35\], and the results are shown in Table 2 and plotted in Figure 4. It can be seen that the shear modulus, Young’s modulus, Poisson’s ratio, Cauchy pressure and anisotropy coefficient for a material, and the material exhibits ductility. On the contrary, covalent bonding plays a dominant role in these alloys and exhibits good ductility. It also shows that the larger the Poisson’s ratio is, the better the plasticity is \[51\]. Since the research method of Poisson’s ratio. Poisson’s ratio (\(\nu\)) is consistent with that of B/G ratio, it will not be repeated.

The Cauchy pressure is negative. The smaller the negative value is, the stronger the covalent bonding is and thus the better ductility is. Conversely, for brittle materials, the more serious the brittleness is. As can be seen from Figure 4d, the Cauchy pressures of all six impurity elements affect the elastic modulus of pure tungsten metal, especially Cu and Ni. This is consistent with the order of shear modulus. To sum up, the impurity elements Cr, Cu, Fe, Mn, Mo and Ni all affect the elastic modulus of pure tungsten metal. As it is shown in Figure 4c, the change trend of Poisson’s ratio is similar to that of B/G ratio, and ductile behavior of materials. The higher the value of B/G is, the better the ductility is, and the critical value is about 1.75. It can be seen from Table 2 that the B/G values of the W-TM alloys are all greater than 1.75 and higher than that of pure tungsten metal, which indicates that the W-TM alloys have good ductility, and that these transition metal impurities can improve the ductility of pure tungsten metal. This is consistent with Pugh theory \[50\], the ratio of (B/G) can be calculated to understand the brittle transition of TM (TM = Cr, Cu, Fe, Mn, Mo and Ni) impurities in W.

Table 2. The elastic constants (C\(_{ij}\)), Cell volumes (V), Lattice constants (LC), Formation energies (\(E_f\)), Cohesive energies (\(E_{coh}\)), Bulk modulus (B), Shear modulus (G), Young’s modulus (E), B/G ratio, Poisson’s ratio (\(\nu\)), Cauchy pressures (C) and Anisotropic coefficients (A) of TM (TM = Cr, Cu, Fe, Mn, Mo and Ni) impurities in W.

| Composition | \(C_{11}\) (GPa) | \(C_{12}\) (GPa) | \(C_{44}\) (GPa) | V (\(\text{Å}^3\)) | LC (\(\text{Å}\)) | \(E_f\) (eV/atom) | \(E_{coh}\) (eV/atom) |
|-------------|------------------|------------------|------------------|-------------------|----------------|-----------------|-------------------|
| Pure W      | 529.937          | 211.189          | 140.594          | 32.022            | 3.1755         | 0.00000         | 8.58829           |
| Experiment  | 533.9 [40]       | 205.1 [40]       | 163.3 [40]       | 3.165 [40]        |                |                 | 8.50110           |
| Theory      | 533 [45]         | 205 [45]         | 163 [45]         | 3.165 [41]        | 0.00324        | 8.46980         | 8.50635           |
| \(W_{53}\)Cr\(_1\) | 522.391          | 210.153          | 136.216          | 31.870            | 3.1705         | 0.00176         | 8.49174           |
| \(W_{53}\)Cu\(_1\) | 508.069          | 211.512          | 136.858          | 31.921            | 3.1722         | 0.01577         | 8.55048           |
| \(W_{53}\)Fe\(_1\)  | 513.013          | 213.208          | 136.862          | 31.850            | 3.1698         | 0.01760         | 8.50305           |
| \(W_{53}\)Mn\(_1\)  | 519.316          | 211.177          | 137.715          | 31.853            | 3.1700         | -0.01173        | 8.49174           |
| \(W_{53}\)Mo\(_1\)  | 523.787          | 210.048          | 136.617          | 32.010            | 3.1751         | -0.00352        | 8.55048           |
| \(W_{53}\)Ni\(_1\)  | 509.806          | 212.978          | 137.574          | 31.871            | 3.1705         | 0.01477         | 8.50091           |

| Composition | B (GPa) | G (GPa) | E (GPa) | B/G | \(\nu\) | C\(_c\) (GPa) | A |
|-------------|---------|---------|---------|------|--------|--------------|---|
| Pure W      | 317.438 | 148.106 | 384.518 | 2.1433 | 0.2981 | 35.2972 | 0.882 |
| \(W_{53}\)Cr\(_1\) | 314.232 | 144.177 | 375.155 | 2.1795 | 0.3010 | 36.9685 | 0.873 |
| \(W_{53}\)Cu\(_1\) | 310.364 | 141.426 | 368.332 | 2.1945 | 0.3022 | 37.3271 | 0.923 |
| \(W_{53}\)Fe\(_1\) | 313.143 | 142.078 | 370.240 | 2.2040 | 0.3029 | 38.1730 | 0.913 |
| \(W_{53}\)Mn\(_1\) | 313.890 | 144.257 | 375.280 | 2.1759 | 0.3007 | 36.7310 | 0.894 |
| \(W_{53}\)Mo\(_1\) | 314.627 | 144.718 | 376.439 | 2.1741 | 0.3006 | 36.7151 | 0.871 |
| \(W_{53}\)Ni\(_1\) | 311.920 | 141.910 | 369.669 | 2.1980 | 0.3025 | 37.7018 | 0.927 |

Figure 4. Elastic constants (a), elastic moduli (b), Poisson’s ratio and B/G ratio (c) and Cauchy pressures (d) of pure W and the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys.

In order to better investigate the mechanical properties of the W-TM alloys, bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio, Cauchy pressure and anisotropy coefficient for a polycrystalline material are deduced from single-crystal elastic constants by using Voigt-Reuss-Hill approximations \[32–35\], and the results are shown in Table 2 and plotted in Figure 4. It can be seen...
from Figure 4b that the bulk modulus of the six alloys is larger than the corresponding shear modulus, indicating that the critical factor of affecting the structural stability is the shear modulus [48]. The bulk modulus is usually used to characterize the ability of a material to resist deformation under applied stress [49,50]. The larger the bulk modulus value is, the stronger the resistance to deformation is. We can see that bulk modulus of six alloys is lower than that of pure tungsten metal, indicating that the ability of these alloys to resist deformation is weakened. The order from strength to weakness is the W-Mo, W-Cr, W-Mn, W-Fe, W-Ni and W-Cu alloy. Similarly, shear modulus is usually used to characterize the ability of a material to resist shear deformation under shear stress [49,50]. The larger the shear modulus value is, the stronger the resistance to shear deformation is. We can see that shear modulus of six alloys is lower than that of pure tungsten metal, indicating that the ability of these alloys to resist shear deformation is weakened. The order from strength to weakness is the W-Mo, W-Mn, W-Cr, W-Fe, W-Ni and W-Cu alloy. Young’s modulus is defined as the ratio of stress to strain, which provides a method to measure the stiffness of solid. The larger the Young’s modulus value is, the greater the material stiffness is. Obviously, we can see that Young’s modulus of six alloys is also lower than that of pure tungsten metal, indicating that the stiffness of these alloys is weakened. The order of stiffness from strength to weakness is the W-Mo, W-Mn, W-Cr, W-Fe, W-Ni and W-Cu alloy. This is consistent with the order of shear modulus. To sum up, the impurity elements Cr, Cu, Fe, Mn, Mo and Ni all affect the elastic modulus of pure tungsten metal, especially Cu and Ni.

Figure 4c shows the ratio of bulk modulus to shear modulus (B/G) and Poisson’s ratio of the W-TM alloys. According to Pugh theory [50], the ratio of (B/G) can be calculated to understand the brittle and ductile behavior of materials. The higher the value of B/G is, the better the ductility is, and the critical value is about 1.75. It can be seen from Table 2 that the B/G values of the W-TM alloys are all greater than 1.75 and higher than that of pure tungsten metal, which indicates that the W-TM alloys have good ductility, and that these transition metal impurities can improve the ductility of pure tungsten metal. Figure 4c also shows that iron element performs well in improving the ductility of tungsten metal, followed by nickel, copper, chromium and manganese, and the worst is molybdenum. As it is shown in Figure 4c, the change trend of Poisson’s ratio is similar to that of B/G ratio. Poisson’s ratio (−1 < ν < 0.5) is usually used to characterize the ability of a crystal against shear, the larger the Poisson’s ratio is, the better the plasticity is [51]. Since the research method of Poisson’s ratio is consistent with that of B/G ratio, it will not be repeated.

Cauchy pressure is usually used to characterize the behavior of metallic bonding and covalent bonding in materials [52]. In general, if the Cauchy pressure is positive, the metallic bonding is dominant in the material, and the material exhibits ductility. On the contrary, covalent bonding plays a dominant role in materials, which show brittleness. The larger the Cauchy pressure value is, the stronger the metallic bonding is and thus the better ductility is. Conversely, for brittle materials, the Cauchy pressure is negative. The smaller the negative value is, the stronger the covalent bonding is and the more serious the brittleness is. As can be seen from Figure 4d, the Cauchy pressures of all six alloys are positive and exceed the Cauchy pressures of pure tungsten metals, indicating that the metallic bonding in these alloys play a dominant role and exhibit good ductility. It also shows that the six impurity elements can improve the ductility of pure tungsten metal. This is consistent with the analysis of B/G ratio and Poisson’s ratio.

In engineering, the degree of anisotropy is expressed by the anisotropy factor A. If A = 1, it means that the material is an isotropic crystal; if A deviates from 1, it means that the material is an anisotropic crystal. The larger the deviation of A is, the more serious the material anisotropy is. As can be seen from Table 2, the anisotropic factors of the W-Cr and W-Mo alloys are all less than that of pure tungsten, while the anisotropic factors of the W-Cu, W-Fe, W-Mn and W-Ni alloys are all greater than that of pure tungsten. It indicates that the impurities Cu, Fe, Mn and Ni can improve the anisotropy of pure tungsten metal, while the impurities Cr and Mo result in more serious anisotropy of pure tungsten metal.
3.5. Melting Point and Hardness

Melting point is a very important parameter in designing new materials. In order to improve the heat resistance of W alloys, it is very important to investigate the melting point. Therefore, the melting points of pure W metal and the W-TM alloys are calculated.

For binary intermetallic compounds, the melting point can be derived by using the cohesive energy, as follows [53]:

$$T_m(K) = 3.84867\left|\frac{E_{coh}(kJ/mol)}{16}\right|$$  \hspace{1cm} (16)

For metallic materials, the melting point can be derived by using the elastic constant $C_{11}$, as follows [54]:

$$T_m = 553K + (5.91 \text{ K/GPa})C_{11} \pm 300K$$  \hspace{1cm} (17)

The melting points of pure W metal and the W-TM alloys are calculated by using the Equations (16) and (17) is shown in Figure 5a. The melting point of tungsten is calculated by using Equation (17) is very close to the actual value (3695 K) [55,56], which shows that our calculation results are credible. It can be seen that the melting point of the W-Mo alloy is the highest except for the melting point of pure W, while that of the W-Cu alloy is the lowest. It indicates that the transition metal Cu impurity has the greatest influence on the melting point of pure W metal, while the transition metal Mo impurity has the least effect. Obviously, the higher the melting point of the alloy, the tighter the atoms is bonded to each other in the crystal lattice.

![Figure 5](image-url)  \hspace{1cm} Figure 5. Melting points (a) and Hardness (b) of pure W and the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys.

3.6. Electronic Structures

In order to further understand the bonding characteristics of the W-TM alloys and reveal its mechanical properties and basic structural stability mechanism, the total density of states (TDOS) of pure W and the W-TM alloys have been calculated. Figure 6 depicts the TDOS with the energy interval from (EF = $-4 \text{ eV}$) up to (EF = $+2 \text{ eV}$). We can see that the density of states at the Fermi level is nonzero, indicating that the W-TM alloys exhibits metallic characteristics. In fact, the main characteristic of electronic structures of the W-TM alloys is the hybridization between W-d and TM-d orbitals. As can be seen from Figure 6, the shape of TDOS curves present a tiny change, which indicates the structures of the W-TM alloys does not undergo dramatic changes and no structural phase transformation occurs. Moreover, TDOS of the W-TM alloys decreases comparing with that of pure W, and the change of interaction potential can be caused by the charge transfer between W and TM atoms. It can also be seen that there is a pseudo-gap near the Fermi level. In general, the larger the pseudo-gap is, the stronger the covalent bonding is [59–61]. This question can be expressed more clearly when the Debye temperature is investigated in Section 3.7. According to the report [62], the decrease or increase of $D_f$ (density of states at the Fermi level) is related to the hardening or softening
As an important parameter, hardness (H) plays an important role in the application of materials, especially for evaluating the wear behavior of materials [57]. It is therefore necessary to investigate the hardness of materials. Hardness can be derived by using Poisson’s ratio and Young’s modulus, as follows [58]:

$$H = \frac{(1-2\nu)E}{6(1+\nu)}$$

(18)

The calculation results of hardness are shown in Figure 5b. It can be seen from the Figure 5b that pure W has the strongest hardness, followed by the W-Mo, W-Mn, W-Cr, W-Ni and W-Fe alloys, and the W-Cu alloy has the worst hardness. The results show that the transition metal Cu impurity has the greatest influence on the hardness of W metal, while the transition metal Mo impurity has the least effect. The result is consistent with the analysis of the melting point above.

3.6. Electronic Structures

In order to further understand the bonding characteristics of the W-TM alloys and reveal its mechanical properties and basic structural stability mechanism, the total density of states (TDOS) of pure W and the W-TM alloys have been calculated. Figure 6 depicts the TDOS with the energy interval from ($E_F = -4$ eV) up to ($E_F = +2$ eV). We can see that the density of states at the Fermi level is nonzero, indicating that the W-TM alloys exhibit metallic characteristics. In fact, the main characteristic of electronic structures of the W-TM alloys is the hybridization between W-d and TM-d orbitals. As can be seen from Figure 6, the shape of TDOS curves present a tiny change, which indicates the structures of the W-TM alloys do not undergo dramatic changes and no structural phase transformation occurs. Moreover, TDOS of the W-TM alloys decreases comparing with that of pure W, and the change of interaction potential can be caused by the charge transfer between W and TM atoms. It can also be seen that there is a pseudo-gap near the Fermi level. In general, the larger the pseudo-gap is, the stronger the covalent bonding is [59–61]. This question can be expressed more clearly when the Debye temperature is investigated in Section 3.7. According to the report [62], the decrease or increase of $D_f$ (density of states at the Fermi level) is related to the hardening or softening of the alloy materials, respectively. Our calculated $D_f$ values of pure W, W-Cr, W-Cu, W-Fe, W-Mn, W-Mo and W-Ni alloys are 27.6546, 26.7746, 16.5274, 46.4710, 30.9737, 27.2641 and 22.1396 electrons/eV, respectively, which indicates the hardness of the W-Cu alloy is the maximum, while that of the W-Fe alloy is the minimum. In addition, it can be seen from Figure 6 that the degree of overlapping of W-states and TM-states in the case of the W-Mo alloy is higher than that of other alloys, indicating that the bonding strength of the W-Mo alloy is higher than that of other alloys. The result is consistent with the analysis of the formation energy.

Besides, the metallicity of the W-TM alloys can be estimated by [17,63,64]:

$$f_m = \frac{n_m}{n_e} = \frac{k_BT D_f}{n_e} = \frac{n_e}{0.026D_f}$$

(19)

where $D_f$ is the TDOS value at the Fermi level in unit states/eV-cell, $k_B$ is the Boltzmann constant, $T$ is the temperature, $n_m$ and $n_e$ are the thermal excited electrons and valence electron density of the cell, respectively. $n_e$ is calculated by $n_e = N/V_{cell}$, $N$ is the total number of valence electrons and $V_{cell}$ is the cell volume. The calculated $f_m$ with pure W and doping Cr, Cu, Fe, Mn, Mo and Ni are 1.9187, 1.8488, 1.1257, 3.1872, 2.1311, 1.8909 and 1.5102, respectively. Obviously, Doping Fe or Mn can improve the metallicity of pure W metal, while doping with chromium, copper, molybdenum and nickel reduces the metallicity of pure W metal, of which the W-Cu alloy has the worst metallicity.
Debye temperature is an important physical quantity of solids, which derives from the atomic thermal vibration theory of solids. It not only reflects the degree of dynamic distortion of crystal lattice, but also characterizes the binding force between atoms. Debye temperature is closely related to many physical properties of solids, such as lattice stability, expansion coefficient, elasticity, specific heat, melting point and hardness. In order to further understand the thermodynamic behaviors and lattice stability of the W-TM alloys with doping different transition elements, it is necessary to calculate the $\Theta_D$ values and know its variation rule. This information is very important for the design and development of these alloy materials. By using the Equations (10)–(13), the values of $v_s$, $v_l$, $v_m$ and $\Theta_D$ are calculated and the results are listed in Table 3.

Table 3. Mass density ($\rho$), molar mass (M), shear sound velocity ($v_s$), longitudinal sound velocity ($v_l$), average wave velocity ($v_m$) and Debye temperatures ($\Theta_D$) of pure W and the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys.

| Composition | $\rho$ (g cm$^{-3}$) | M (g/mol) | $v_s$ (m s$^{-1}$) | $v_l$ (m s$^{-1}$) | $v_m$ (m s$^{-1}$) | This Work | Ref. [65] |
|-------------|-------------------|---------|------------------|------------------|------------------|----------|----------|
| Pure W      | 19.0738           | 183.8400| 2786.56          | 5195.75          | 3111.78          | 367.579  | 333.4    |
| $W_{53}$Cr$_1$ | 18.9097           | 181.3984| 2761.25          | 5175.28          | 3084.65          | 364.949  | —        |
| $W_{53}$Cu$_1$ | 18.9015           | 181.6122| 2735.38          | 5137.75          | 3056.21          | 361.389  | —        |
| $W_{53}$Fe$_1$ | 18.9288           | 181.4696| 2739.70          | 5152.78          | 3061.32          | 362.263  | —        |
| $W_{53}$Mn$_1$ | 18.9251           | 181.4529| 2760.89          | 5171.97          | 3084.14          | 364.951  | —        |
| $W_{53}$Mo$_1$ | 18.9117           | 182.2122| 2766.28          | 5180.71          | 3090.11          | 365.062  | —        |
| $W_{53}$Ni$_1$ | 18.9220           | 181.5224| 2738.57          | 5146.28          | 3059.88          | 362.014  | —        |

The $\Theta_D$ of pure W metal at 0 K is obtained to be about 367.597 K, which is close to the result 333.4 K [65]. There is an error of 10.26% between the two. This is because the model used in [65] is the Debye-Gruneisen model, but the elastic constant is used in this paper. The two data are basically consistent, which confirms that the results are credible in this paper. It can be also seen that the calculated $\Theta_D$ values of the W-TM alloys with doping Cr, Cu, Fe, Mn, Mo and Ni are 364.949 K, 361.389 K, 362.263 K, 364.951 K, 365.062 K, and 362.014 K, respectively. The $\Theta_D$ values of these alloys...
are lower than that of pure tungsten. As we all know that the Θ_D can be used to describe the covalent bonding strength of solids. Therefore, the covalent bonding strength of the W-TM alloys is lower than that of pure tungsten metal. Meanwhile, the covalent bonding strength of the W-TM alloys decreases with doping Mo, Mn, Cr, Fe, Ni and Cu, successively, which is consistent with the analysis of electronic structure.

4. Summaries and Conclusions

In this paper, the phase stability, elastic properties, melting point and hardness, electronic properties and Debye temperature of the W-TM (TM = Cr, Cu, Fe, Mn, Mo and Ni, respectively) alloys are investigated by the first principle method. The main conclusions are as follows:

1. The W-TM alloys still maintain the bcc lattice, and have no structural phase transformation. Of note, however, the lattice constants of the W-Cu and W-Ni alloys are anomalous than that of other alloys. The lattice constants of the W-Cu and W-Ni alloys are higher than that of the W-Cr, W-Fe and W-Mn alloys.

2. The W-Mo and W-Mn alloys have better alloying ability with strong interactions between W and Mo/Mn atoms. However, the alloying ability of the W-Cu, W-Fe, W-Cr and W-Ni is poor, and there is a weak chemical interaction between W and Cu/Cr/Fe/Ni atoms.

3. The impurity elements Cr, Cu, Fe, Mn, Mo and Ni all affect the mechanical strength of pure tungsten metal, especially Cu and Ni. Fe element performs well in improving the ductility of pure W metal, followed by Ni, Cu, Cr and Mn, and the worst is Mo. The impurities Cu, Fe, Mn and Ni can improve the anisotropy of pure tungsten metal, while the impurities Cr and Mo result in more serious anisotropy of pure tungsten metal.

4. The transition metal Cu impurity has the greatest influence on the melting point and hardness of pure W metal, while the transition metal Mo impurity has the least effect.

5. The metallic bonding of the W-TM alloys is strengthened while covalent bonding is reduced. The metallicity of pure W metal can be enhanced by doping it with Fe or Mn, while doping with Cr, Cu, Mo and Ni reduces the metallicity of pure W metal, of which the W-Cu alloy has the worst metallicity.

Author Contributions: D.J., M.W., D.L., F.L., M.C. and S.L. conceived and designed the study. D.J. performed the computational calculations and drafted the paper. M.W., D.L., F.L., M.C. and S.L. reviewed and edited the manuscript. All authors contributed to explain the results, read and approve the manuscript.

Funding: This study is supported by the International Science and Technology Cooperation Program of China (Grant No. 2015DFA61800) and the Scientific Research Fund of Jiangxi Provincial Education Department (Grant No. GJJ180973).

Acknowledgments: The author Diyou Jiang would like to thank the computing team led by Chuying Ouyang of Jiangxi Normal University. The utilization of the computing facilities at the Computational Materials Laboratory is also acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tanabe, T.; Noda, N.; Nakamura, H. Review of high Z materials for PSI applications. J. Nucl. Mater. 1992, 196, 11–27. [CrossRef]
2. Garcia-Rosales, C. Erosion processes in plasma-wall interactions. J. Nucl. Mater. 1994, 211, 202–214. [CrossRef]
3. Chuyanov, V.A. ITER EDA project status. J. Nucl. Mater. 1996, 233, 4–8. [CrossRef]
4. Ekman, M.; Persson, K.; Grimvall, G. Phase diagram and lattice instability in tungsten rhenium Alloys. J. Nucl. Mater. 2000, 278, 273–276. [CrossRef]
5. Kim, Y.D.; Oh, N.L.; Oh, S.T.; Moon, I.H. Thermal conductivity of W-Cu composites at various Temperatures. Mater. Lett. 2001, 51, 420–424. [CrossRef]
6. Dosovitskiy, G.A.; Samoilenkov, S.V. Thermal expansion of Ni-W, Ni-Cr, and Ni-Cr-W alloys between room temperature and 800 degrees c. *Int. J. Thermophys.* 2009, 30, 1931–1937. [CrossRef]

7. Liu, B.X.; Huang, L.J.; Geng, L.; Wang, B.; Liu, C.; Zhang, W.C. Fabrication and superior ductility of laminated Ti-TiB2/Ti composites by diffusion welding. *J. Alloys Compd.* 2014, 602, 187–192. [CrossRef]

8. Mutoh, Y.; Ichikawa, K.; Nagata, K.; Takeuchi, M. Effect of rhenium addition on fracture toughness of tungsten at elevated temperatures. *J. Mater. Sci.* 1995, 30, 770–775. [CrossRef]

9. Jiang, D.Y.; Ouyang, C.Y.; Liu, S.Q. Mechanical properties of W-Ti alloys from first-principles Calculations. *Fusion Eng. Des.* 2016, 106, 34–39.

10. Jiang, D.Y.; Wang, Q.L.; Hu, W.; Wei, Z.Q.; Tong, J.B.; Wan, H.Q. The effect of tantalum (Ta) doping on mechanical properties of tungsten (W): A first-principles study. *J. Mater. Res.* 2016, 31, 3401–3408. [CrossRef]

11. Jiang, D.Y.; Zhou, Q.; Xue, L.; Wang, T.; Hu, J.F. First-principles study the phase stability and mechanical properties of binary W-Mo alloys. *Fusion Eng. Des.* 2018, 130, 56–61. [CrossRef]

12. Jiang, D.Y.; Wang, T.; Huang, X.H.; Zou, X.Z.; Hu, J.F. Effect of Hf additions on phase stability and mechanical properties of binary W-Hf alloys: A first-principles study. *Fusion Eng. Des.* 2018, 137, 295–302. [CrossRef]

13. Jiang, D.Y.; Zhou, Q.; Liu, W.H.; Wang, T.; Hu, J.F. First-principles study the structures and mechanical properties of binary W-V alloys. *Phys. B Condens. Matter* 2019, 552, 165–169. [CrossRef]

14. Jiang, D.Y.; Xue, L.; Huang, X.M.; Wang, T.; Hu, J.F. Effect of Zr additions on crystal structures and mechanical properties of binary W-Zr alloys: A first-principles study. *J. Mater. Res.* 2019, 34, 290–300.

15. Fukuzumi, S.; Yoshiie, T.; Satoh, Y.; Xu, Q.; Mori, H.; Kawai, M. Defect structural evolution in high purity tungsten irradiated with electrons using high voltage electron microscope. *J. Nucl. Mater.* 2005, 343, 308–312. [CrossRef]

16. Kong, X.S.; Wu, X.B.; You, Y.W.; Liu, C.S.; Fang, Q.F.; Chen, J.L.; Luo, G.N.; Wang, Z.G. First-principles calculations of transition metal-solute interactions with point defects in tungsten. *Acta Mater.* 2014, 66, 172–183. [CrossRef]

17. Qi, L.; Jin, Y.C.; Zhao, Y.H.; Yang, X.M.; Zhao, H.; Han, P.D. The structural, elastic, electronic properties and Debye temperature of Ni3Mo under pressure from first-principles. *J. Alloys Compd.* 2015, 621, 383–388. [CrossRef]

18. Chen, Q.; Huang, Z.W.; Zhao, Z.D.; Hu, C.K. Thermal stabilities, elastic properties and electronic structures of B2-MgRE (RE = Sc, Y, La) by first-principles calculations. *Comput. Mater. Sci.* 2013, 67, 196–202. [CrossRef]

19. Muzyk, M.; Nguyen-Manh, D.; Kurzydłowski, K.J.; Baluc, N.L.; Dudarev, S.L. Phase stability, point defects, and elastic properties of W-V and W-Ta alloys. *Phys. Rev. B* 2011, 84, 104115. [CrossRef]

20. Hu, Y.J.; Shang, S.L.; Wang, Y.; Darling, K.A.; Butler, B.G.; Kecskes, L.J.; Liu, Z.K. Effects of alloying elements and temperature on the elastic properties of W-based alloys by first-principles calculations. *J. Alloys Compd.* 2016, 671, 267–275. [CrossRef]

21. Giusepponi, S.; Celino, M. The ideal tensile strength of tungsten and tungsten alloys by first-principles calculations. *J. Nucl. Mater.* 2013, 435, 52–55. [CrossRef]

22. Muzyk, M.; Nguyen-Manh, D.; Wrobel, J.; Kurzydłowski, K.J.; Baluc, N.L.; Dudarev, S.L. First-principles model for phase stability, radiation defects and elastic properties of W-Ta and W-V alloys. *J. Nucl. Mater.* 2013, 442, S680–S683. [CrossRef]

23. Wei, N.; Jia, T.; Zhang, X.L.; Liu, T.; Zeng, Z.; Yang, X.Y. First-principles study of the phase stability and the mechanical properties of W-Ta and W-Re alloys. *AIP Adv.* 2014, 4, 057103. [CrossRef]

24. Bertoldi, D.S.; Ramosa, S.B.; Guillermet, A.F. Interrelations between EOS parameters and cohesive energy of transition metals: Thermostatistical approach, ab initio calculations and analysis of “universality” features. *J. Phys. Condens. Matter* 2017, 107, 93–97. [CrossRef]

25. Kresse, G.; Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* 1993, 48, 13115. [CrossRef] [PubMed]

26. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, 11169. [CrossRef] [PubMed]

27. Böhm, P.E. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953. [CrossRef] [PubMed]

28. Wang, Y.; Perdew, J.P. Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling. *Phys. Rev. B* 1991, 44, 13298. [CrossRef] [PubMed]

29. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188. [CrossRef]
30. Wallace, D.C. Thermoelastic Theory of Stressed Crystals and Higher-Order Elastic Constants. Solid State Phys. 1970, 25, 301–404.

31. Zhao, J.; Winey, J.M.; Gupta, Y.M. First principles calculations of second- and third-order elastic constants for single crystals of arbitrary symmetry. Phys. Rev. B 2007, 75, 094105. [CrossRef]

32. Voigt, W. über die Beziehung zwischen den beiden Elasticitäts constanten isotroper Körper. Ann. Physik 1889, 38, 573–587. [CrossRef]

33. Reuss, A. Berechnung der Fließgrenze von Mischkristallen auf Grupdf der Plastizitäts bedingung für Einkristalle. Zamm Z. Angew. Math. Mech. 1929, 9, 49–58. [CrossRef]

34. Hill, R. The elastic behaviour of a crystalline aggregate. Phys. Soc. Lond. Sect. A 1952, 65, 349–354. [CrossRef]

35. Hill, R. Elastic properties of reinforced solids: Some theoretical principles. J. Mech. Phys. Solids 1963, 11, 357–372. [CrossRef]

36. Anderson, O.L. A simplified method for calculating the Debye temperature from elastic constants. J. Phys. Chem. Solids 1963, 24, 909–917. [CrossRef]

37. Wachtler, P.; Filzmoser, M.; Rebizant, J. Electronic and elastic properties of the light actinide tellu-rides. Physica B 2001, 293, 199–223. [CrossRef]

38. Jin, S.; Liu, Y.L.; Zhou, H.B.; Zhang, Y.; Lu, G.H. First-principles investigation on the electronic and mechanical properties of Ti-24Nb-4Zr-SSn single crystals with bcc crystal structure. Acta Mater. 2011, 59, 3081–3090. [CrossRef]

39. Kittel, B.C. Introduction to Solid State Physics, 7th ed.; Wiley: New York, NY, USA, 1996.

40. Featherston, F.H.; Neighbors, J.R. Elastic Constants of tantalum, tungsten, and molybdenum. Phys. Rev. 1963, 130, 1324. [CrossRef]

41. Sahu, B.R. Electronic structure and bonding of ultralight LiMg. Mater. Sci. Eng. B 1997, 49, 74–78. [CrossRef]

42. Didukh, L. 3d-electrons contribution to cohesive energy of 3d-metals. Condens. Matter Phys. 2018, 21, 13701. [CrossRef]

43. Zhang, Y.W.; Li, S.J.; Obbard, E.G.; Wang, H.; Wang, S.C.; Hao, Y.L.; Yang, R. Elastic properties of Ti-24Nb-4Zr-SSn single crystals with bcc crystal structure. Acta Mater. 2011, 59, 3081–3090. [CrossRef]

44. Soderlind, P.; Eriksson, O.; Wills, J.M.; Boring, A.M. Theory of elastic constants of cubic transition metals and alloys. Phys. Rev. B 1993, 48, 5844–5851. [CrossRef] [PubMed]

45. Einarsdotter, K.; Sadigh, B.; Grimvall, G.; Ozolins, V. Phonon Instabilities in fcc and bcc Tungsten. Phys. Rev. B 2007, 76, 054115. [CrossRef]

46. Wu, Z.J.; Zhao, E.J.; Xiang, H.P.; Hao, X.F.; Liu, X.J.; Meng, J. Crystal structures and elastic properties of Ti-24Nb-4Zr-SSn single crystals with bcc crystal structure. Acta Mater. 2011, 59, 3081–3090. [CrossRef]

47. Lin, J.J.; Winey, J.M.; Gupta, Y.M. First principles calculations of second- and third-order elastic constants for single crystals of arbitrary symmetry. Phys. Rev. B 2007, 75, 094105. [CrossRef]

48. Liu, Q.J.; Liu, Z.T.; Feng, L.P.; Tian, H. First-principles study of structural, elastic, electronic and optical properties of orthorhombic NaAlF4. Comput. Mater. Sci. 2011, 50, 2822–2827. [CrossRef]

49. Meradjil, H.; Drabila, S.; Chemid, S. First-principles elastic constants and electronic structure of BP, BAs, and BSb. Phys. Status Solidi B 2004, 241, 2881–2885. [CrossRef]

50. Pugh, S.F. Relations between the elastic moduli and the plastic properties of polycrystalline pure Metals. Philos. Mag. A 1954, 45, 823–843. [CrossRef]

51. Cao, Y.; Zhu, J.C.; Liu, Y.; Nong, Z.S.; Li, Z.H. First-principles studies of the structural, elastic, electronic and thermal properties of Ni3Si. Comput. Mater. Sci. 2013, 69, 40–45. [CrossRef]

52. Tang, B.Y.; Yu, W.Y.; Zeng, X.Q.; Ding, W.J.; Gray, M.F. First-principles study of the electronic structure and mechanical properties of CaMg2 Laves Phase. Mater. Sci. Eng. A 2008, 489, 444–450. [CrossRef]

53. Li, C.H.; Hoe, J.L.; Wu, P. Empirical correlation between melting temperature and cohesive energy of binary Laves Phases. J. Phys. Chem. Solids 2003, 64, 201–212. [CrossRef]

54. Xu, S.H.; Zhang, F.Q.; Feng, P.; Liu, J.S. First-principles calculations of structural stabilities and elastic properties of AB2 type intermetallics in ZA62 magnesium alloy. Acta Met. Sin. 2010, 46, 97–103.

55. Coenen, J.W.; Philipps, V.; Brezinsek, S.; Pintsuk, G.; Tanabe, T.; Ueda, Y.; Samm, U.; TEXTOR Team. Analysis of structural changes and high-heat-flux tests on pre-damaged tungsten from tokamak melt experiments. Phys. Scr. 2011, T145, 014066. [CrossRef]

56. Coenen, J.W.; Arnoux, G.; Bazylev, B.; Matthews, G.F.; Autricque, A.; Balboa, I.; Clever, M.; Dejarnac, R.; Coffey, I.; Corre, Y.; et al. ELM-induced transient tungsten melting in the JET divertor. Nucl. Fusion 2015, 55, 023010. [CrossRef]
57. Richardson, R.C.D. The wear of metals by hard abrasives. *Wear* **1967**, *10*, 291–309. [CrossRef]
58. Ji, Z.W.; Hu, C.H.; Wand, D.H. Mechanical Properties and chemical bonding of the Os-B system: A first-Principles study. *Acta Mater.* **2012**, *60*, 4208–4217. [CrossRef]
59. Shi, Y.J.; Du, Y.L.; Chen, G.; Chen, G.L. First principle study on phase stability and electronic structure of YCu. *Phys. Lett. A* **2007**, *368*, 495–498. [CrossRef]
60. Hu, Q.M.; Yang, R.; Xu, D.S.; Hao, Y.L.; Li, D.; Wu, W.T. Energetics and electronic structure of grain boundaries and surfaces of B- and H-doped Ni3Al. *Phys. Rev. B* **2003**, *67*, 224203. [CrossRef]
61. Yang, X.M.; Hou, H.; Zhao, Y.H.; Yang, L.; Han, P.D. Preparation of lamellar carbon matrix for sulfur as cathode material of lithium-sulfur batteries. *Comput. Mater. Sci.* **2014**, *84*, 374–382. [CrossRef]
62. Yan, M.F.; Chen, H.T. Structural, elastic and electronic properties of Cr2N: A first-principles study. *Comput. Mater. Sci.* **2014**, *88*, 81–85. [CrossRef]
63. Li, Y.F.; Gao, Y.M.; Xiao, B. Theoretical study on the stability, elasticity, hardness and electronic structures of W-C binary compounds. *J. Alloys Comp.* **2010**, *502*, 28–37. [CrossRef]
64. Huang, Z.W.; Zhao, Y.H.; Hou, H.; Han, P.D. Electronic structural, elastic properties and thermodynamics of Mg17Al12, Mg2Si and A12Y phases from first-principles calculations. *Physica B* **2012**, *407*, 1075–1081. [CrossRef]
65. Yu, C.F.; Jiang, X.F.; Cheng, P.F.; Zhu, C.J. Correlations among linear expansion coefficient, Debye temperature and Young’s modulus of metals. *Phys. Exp.* **2012**, *32*, 37–40.

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).