Effects of alloying elements and temperature on the elastic properties of W-based alloys by first-principles calculations

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Abstract

The influence of various transition alloying elements (X's) on the elastic properties of W-based alloys has been studied via first-principles calculations on the basis of density functional theory. Here, nineteen transition metal alloying elements (X) are considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. It is found that (i) the bulk modulus of the dilute W-X alloy decreases with increasing its equilibrium volume, particularly, for the alloying elements in the same period; (ii) all of the alloying elements decrease the shear modulus of BCC W; and (iii) the largest decrease of elastic properties of W is due to alloying element Y. In addition, it is shown that the changes of elastic properties of W caused by the alloying elements are traceable from the electron charge density distribution, resulting in a bonding distortion between W and the alloying atoms. Using the quasi-static approach based on the Debye model, the elastic properties of these W-X alloys at finite temperatures are predicted. Calculated properties of BCC W and the W-X alloys are in favorable agreement with available experimental measurements.

Keywords:

First-principles calculations; Tungsten-based alloys; Elastic properties; Quasi-static approach; Electronic structure

1. Introduction

W-based alloys have high melting temperatures, high density, high strength and good resistance to gamma and neutron radiations [1]. Currently, in order to further increase its toughness and ductility, similar to that used in Ni-based superalloys [2], the primary alloying element for BCC W has been Re [1,3,4]. However, Re is one of the least abundant elements in the Earth's crust, resulting in its extremely high price [2]. In response to this dilemma, there is significant on-going research to identify alternative alloying elements for the development of W-based alloys with similar or improved mechanical properties. However, it is likely that the use of other not-yet-tried alloying additions would lead to more complex compositions. Therefore, it is desirable to gain a fundamental understanding of systematic alloying effects on the mechanical properties of W, as a function of temperature. In the present work, we select elasticity for study, as it is hypothesized that the early stage of deformation which reflects the material's capability to recover its original shape after mechanical loading. In addition, the elasticity of single crystals and the associated polycrystalline aggregate properties can provide information about a vast number of material-related behaviors, such as mechanical anisotropy and stability [5], Debye temperature [6], hardness [7], melting temperatures [8], ductility/brittleness [9], and creep rate [10].

Although first-principles approaches based on density functional theory have been proven to be a reliable and efficient method in predicting elastic properties of various alloying systems [5,8,11–13], little work has been performed on the elastic properties of W and its alloys in a comprehensive manner, especially at finite temperatures. Through first-principles calculations, the present work aims to close this gap in understanding by investigating systematically the effects of alloying elements (X's) on the elastic properties of BCC W, as a function of

temperature, including isothermal and isentropic elastic stiffness components, bulk modulus, shear moduli, Young's modulus, and elastic anisotropy. Nineteen transition metal alloying elements are considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. In addition, the trends, regularities of the predicted elastic properties, and their electronic origins are discussed.

2. Computational Methodology

2.1 First-Principles Elastic Properties at 0 K

First-principles elastic stiffness constants of a series of W-1.85 at.% X solid solutions are calculated by using the Vienna Ab-initio Simulation Package (VASP) [14]. A bcc $3 \times 3 \times 3$ supercell comprised of 53 W atoms and one additional atom associated with alloying element X is used. Further, the projector augmented wave method (PAW) [15] and the exchange-correlation functional depicted by the generalized gradient approximation (GGA-PW91) are employed [16]. The energy cutoff of the plane wave is set as 350 eV. For all the calculations, the supercells are relaxed by the Methfessel-Paxton method [17]. The Brillouin-zone integration is performed by using a tetrahedron method with Blöchl corrections [18] and a Monkhorst-Pack k -points grid of $8 \times 8 \times 8$ [17]. The energy convergence criterion of the electronic self-consistency is set as 10^{-6} eV/atom for all of the calculations. The contour plots of the differential charge density are generated using VESTA [19,20].

Elastic stiffness constants in the present work are calculated based on the efficient stress-strain method [21]. Specifically, independent sets of strains are applied to deform the supercell in the elastic range. For a given set of strains, $\boldsymbol{\varepsilon}_i = (\varepsilon_{i,1}, \varepsilon_{i,2}, \dots, \varepsilon_{i,6})$, lattice vectors of the strained supercell, $\mathbf{R}'$, in Cartesian coordinates can be calculated as,

$$\text{Equation 1} \quad \mathbf{R}' = \mathbf{D}\mathbf{R} = \begin{pmatrix} 1 + \varepsilon_{i,1} & \varepsilon_{i,6}/2 & \varepsilon_{i,5}/2 \\ \varepsilon_{i,6}/2 & 1 + \varepsilon_{i,2} & \varepsilon_{i,4}/2 \\ \varepsilon_{i,5}/2 & \varepsilon_{i,4}/2 & 1 + \varepsilon_{i,3} \end{pmatrix} \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{pmatrix}$$

where $\mathbf{R}$ are the lattice vectors of the unstrained supercell. The stresses in response to the given strains are calculated via the aforementioned first-principles approach.

Generally, in order to calculate the complete elastic stiffness constants, six independent sets of strains are applied on the structure:

$$\text{Equation 2} \quad \begin{pmatrix} \varepsilon_{1,1} & \varepsilon_{1,6} \\ \varepsilon_{2,1} & \varepsilon_{2,6} \\ \varepsilon_{3,1} & \dots & \varepsilon_{3,6} \\ \varepsilon_{4,1} & \varepsilon_{4,6} \\ \varepsilon_{5,1} & \varepsilon_{5,6} \\ \varepsilon_{6,1} & \varepsilon_{6,6} \end{pmatrix} = \begin{pmatrix} x & & & & & \\ & x & & & & \\ & & x & & & \\ & & & x & & \\ & & & & x & \\ & & & & & x \end{pmatrix}$$

where $x = \pm 0.01$ in the present work, and the strain components not shown are zero. Using the six sets of corresponding stresses from first-principles, the elastic stiffness constants at a fixed volume, $c_{ij}(V)$, can be determined based on Hooke's law as follows:

$$\text{Equation 3} \quad \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{pmatrix} = \begin{pmatrix} \sigma_{1,1} & \sigma_{1,6} \\ \sigma_{2,1} & \sigma_{2,6} \\ \sigma_{3,1} & \dots & \sigma_{3,6} \\ \sigma_{4,1} & \sigma_{4,6} \\ \sigma_{5,1} & \sigma_{5,6} \\ \sigma_{6,1} & \sigma_{6,6} \end{pmatrix} \begin{pmatrix} \varepsilon_{1,1} & \varepsilon_{1,6} \\ \varepsilon_{2,1} & \varepsilon_{2,6} \\ \varepsilon_{3,1} & \dots & \varepsilon_{3,6} \\ \varepsilon_{4,1} & \varepsilon_{4,6} \\ \varepsilon_{5,1} & \varepsilon_{5,6} \\ \varepsilon_{6,1} & \varepsilon_{6,6} \end{pmatrix}^{-1}$$

For cubic crystals, there are only three independent elastic stiffness constants, c_{11} , c_{12} , and c_{44} . Therefore, instead of six, only two linearly independent sets of strains are needed to calculate all the cubic elastic stiffness constants. In the present work, c_{11} and c_{12} are obtained from the set of strains, ε_1 , and c_{44} is obtained from the set of strains, ε_4 .

Based on the single crystal elastic stiffness constants obtained, aggregate properties of the bulk (B), shear (G), and Young's (E) moduli and Poisson's ratio (ν) associated with polycrystals are estimated by means of the Voigt approximation [22]; this provides the upper bound of elastic properties in terms of uniform strains. For a cubic crystal,

$$\text{Equation 4} \quad B = (c_{11} + 2c_{12})/3$$

$$\text{Equation 5} \quad G = (c_{11} - c_{12} + 3c_{44})/5$$

$$\text{Equation 6} \quad E = 9BG/(3B + G)$$

$$\text{Equation 7} \quad \nu = (3B - 2G)/2(3B + G)$$

The shear modulus along the closest-packed $\langle 111 \rangle$ direction is also calculated since this is the shearing direction for dislocation glide in BCC W [1]. For cubic crystals [23],

$$\text{Equation 8} \quad G_{111} = \frac{3c_{44}(c_{11} - c_{12})}{c_{11} - c_{12} + 4c_{44}}$$

The universal elastic anisotropy index, A^U , can be calculated based on the Zener anisotropy ratio, A^Z . For a cubic crystal [11],

$$\text{Equation 9} \quad A^U = \frac{6}{5} \left(\sqrt{A^Z} - \frac{1}{\sqrt{A^Z}} \right)^2$$

where $A^Z = 2c_{44}/(c_{11} - c_{12})$ [5]. $A^U = 0$ or $A^Z = 1$ indicates an isotropic crystal.

2.2 Thermodynamic and Elastic Properties at Finite Temperatures

The elastic stiffness constants at finite temperatures could be estimated by a quasi-static approach in terms of the predicted Helmholtz free energy at finite temperatures and the predicted elasticity as a function of volume at 0 K [24]. The Helmholtz free energy, $F(V,T)$, at volume V and temperature T can be calculated using the quasi-harmonic approach [25],

$$\text{Equation 10} \quad F(V,T) = E(V) + F_{ele}(V,T) + F_{vib}(V,T)$$

The first part, $E(V)$, is a static energy at 0 K and, without the contribution of the zero-point vibration, it is obtained by a fitting of the first-principles energy vs. volume data points based on a four-parameter Birch-Murnaghan equation of state (EOS) [5,25],

$$\text{Equation 11} \quad E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}$$

where a , b , c and d are fitting parameters from which the equilibrium energy (E_0), volume (V_0) bulk modulus (B_0), and the first derivative of bulk modulus with respect to pressure (B'_0) can be estimated. In the present work, six data points are generally used for the EOS fitting for each alloy. The second part in the Equation 10, $F_{ele}(V,T)$, represents the thermal electronic contribution which is calculated from the electronic density of states (DOS) obtained from first-principles calculations [25,26]. This part is necessary due to the non-zero electronic density at the Fermi level associated with metals. The third part, $F_{vib}(V,T)$, is the contribution of lattice vibrations to the Helmholtz free energy. In the present work, for sake of simplicity and efficiency, the vibrational contribution is depicted based on the Debye-Grüneisen model [25],

$$\text{Equation 12} \quad F_{vib}(V,T) = \frac{9}{8}k_B\Theta_D + k_BT \left\{ 3 \ln \left[1 - \exp \left(-\frac{\Theta_D}{T} \right) \right] - D \left(\frac{\Theta_D}{T} \right) \right\}$$

where k_B is the Boltzmann constant and $D(\Theta_D/T)$ the Debye function. The Debye temperature Θ_D can be calculated by,

Equation 13

$$\Theta_D = s(6\pi^2)^{\frac{1}{3}} \frac{\hbar}{k_B} V_0^{\frac{1}{6}} (B_0/M)^{\frac{1}{2}} (V/V_0)^\gamma$$

where M is the atomic mass and s a scaling factor which is calculated based on the Poisson's ratio of pure W [6]. The Grüneisen constant, γ , is defined as $\gamma = [(1 + B'_0)/2 - x]$, with $x = 2/3$ due to the high melting temperature of W [25].

As temperature and volume are two independent variables of the Helmholtz free energy, the equilibrium volume at temperatures of interests, $V(T)$, can be directly calculated from Equation 10. Combining this with the predicted elastic constants $c_{ij}(V)$, the isothermal elastic stiffness constants at finite temperatures can be estimated as $c_{ij}(T) = c_{ij}(V(T))$ [11,24]. It should be mentioned that this approach assumes that the change of elastic stiffness mainly depends on the volume expansion and anharmonicity effects and contributions due to the fluctuation of microscopic stress tensors are not taken into consideration.

Generally, measured elastic constants obtained via the resonance method are isentropic because the elastic waves travel faster than the rate of heat conduction, leading to the measurements being adiabatic in nature. Therefore, in order to compare them with experiments, the calculated isothermal elastic stiffness constants need to be converted to the isentropic ones. For cubic crystals, the thermodynamic relationships between the isothermal c_{ij}^T and isentropic c_{ij}^S are as follows [27],

Equation 14

$$c_{11}^S/c_{11}^T = c_{12}^S/c_{12}^T = C_P/C_V \quad \text{and} \quad c_{44}^S = c_{44}^T$$

where C_P and C_V are heat capacities at constant pressure and constant volume, respectively, which can be estimated from Helmholtz free energy given in Equation 10[25].

3. Results and Discussion

In this section, we first report the regularities of elastic properties and their electronic origins for the specific W-X alloys at 0 K (Sec. 3.1). Second, we present the elasticity of the W-X alloys at finite temperatures (Sec. 3.2).

3.1 Elastic Properties at 0 K

Table 1 summarizes the calculated elastic properties of the W-X alloys at 0 K as well as the equilibrium volumes and lattice parameters predicted by the EOS fitting. It is found that the present prediction of equilibrium volume of BCC W agrees well with experimental data and previous calculations [5,28]. For the elastic stiffness components, the present c_{11} and c_{12} values are in good agreement with the experimental data at 4.2 K [28], with the largest difference less than 6% for c_{12} . The calculated c_{44} value in the present work has a 12% deviation compared to the experimental data, but it agrees well with a previous calculation [5].

To investigate the lattice distortion induced by the solute atoms, Figure 1 plots the EOS predicted equilibrium volumes from Table 1 compared to the values calculated based on Vegard's law for pure elements with a BCC structure [5]. It is shown that the effect of X on the volume of the dilute W-X alloys can be represented as a mechanical intermixing for the alloying elements which have atomic volumes close to BCC W. Deviation between the first-principles calculation and the prediction from Vegard's law is found when the alloying element has a large disparity of its atomic volume compared to that of BCC W. On one hand, smaller alloying elements lead to positive deviations, such as those of Ni and Co. On the other hand, large negative deviations are found for alloying elements Y, Zr, and Hf, which all have much larger atomic volumes than BCC W. The large deviations from Vegard's law indicate that strong

interactions exist between these solute elements and W, in addition to the mechanical mixing between them. Such interactions can be ascribed to the change of the local electronic environment of the solute atom when it is substituted for a W atom in the BCC W matrix [29].

For dilute solid solutions, the changes of lattice parameter can be approximated as a linear function of alloying concentration [30],

Equation 15
$$a_{W_{53}X} = a_{W_{54}} + k_X x_X$$

where $a_{W_{53}X}$ and $a_{W_{54}}$ are the lattice parameters of the W-X solutions and pure W, respectively, x_X is the mole fraction of alloying elements, and k_X is defined as a linear regression coefficient for element X. Calculated lattice parameters of the W-X solutions and the corresponding linear regression coefficients are listed in Table 1. Figure 2 plots the linear regression coefficients vs. the lattice parameters of alloying elements with the BCC crystal structure. Available experimental values, obtained by a fitting of experimental lattice parameters [31,32], are also included, showing a good agreement. It is found that the linear regression coefficients are generally proportional to the lattice parameters of the alloying elements in the BCC structure. However, Ti and Y are slightly off the observed trend.

To illustrate the effect of alloying elements on the elastic modulus of BCC W, Figure 3 displays the calculated bulk moduli and compares them to those obtained from a linear combination of the pure elemental moduli in the BCC structure in terms of their mole fractions. For most alloying elements studied, it is found that the bulk modulus of the W-X dilute alloy can be approximated as a mechanical mixing of the bulk moduli of X and W. However, similar to the volume analysis described in Figure 1, deviations from this trend are observed for Y, Zr, and Hf, scaling with their respective atomic numbers, which, by the way, all have the HCP structure and

possess fewer valence electrons than W. However, it is noted that no clear correlation is found between the shear moduli of the W-X dilute alloys and those of the pure alloying elements with a BCC structure.

Previously, it has been shown that elastic moduli are generally correlated to equilibrium volume [5,11,12]. Therefore, the calculated polycrystalline bulk and shear moduli of the $W_{53}X$ alloys are plotted as a function of the equilibrium volume of alloys in Figure 4a and 4b. As seen in Figure 4a, the alloys with smaller equilibrium volumes have larger bulk moduli. In addition, within each group of 3d, 4d, and 5d alloying elements, it is found that the bulk modulus of $W_{53}X$ decreases linearly with increasing equilibrium volume. Such trend was also reported for Ni- and Mg-based alloys [11,12]. Other than that for the bulk modulus, no clear correlation can be found between shear modulus and equilibrium volume, as is shown in Figure 4b. It is observed that all of the alloying elements decrease the shear modulus of BCC W to some extent. More precisely, the alloying effects on the shear modulus are found to correlate with the number of the valence electrons of the alloying elements, as shown in Figure 5. For the alloying elements of Cr and Mo with the same numbers of valence electrons as W, the reductions of shear modulus are not significant compared to the other alloying elements. For the elements containing 3 and 5 electrons in their d orbital, respectively, such as V, Nb, Ta, Fe, Ru, and Os, the effect of alloying on shear modulus is moderate. As the disparity of the number of the valence electrons between the alloying element and W becomes larger, the shear modulus of BCC W decreases further. For example, there is a significant decrease of the shear modulus of BCC W alloying with Y, Zr, and Pd. A similar trend is also observed for the shear modulus along the $\langle 111 \rangle$ direction (G_{111}). Since valence electrons are crucial to the formation of chemical bonds, this trend implies that

alloying effects on the shear modulus of W can be understood in terms of the interatomic bonds between the W and the solute atoms. Detailed discussion is provided in a later paragraph.

The elastic deformation behavior of crystalline materials originates from the stretching of atomic bonds when a force is applied. For example, the bulk modulus, which represents the compressibility of a crystal under hydrostatic pressure, is generally related to the stiffness of the chemical bonds. Therefore, it is interesting and important to investigate the electronic origins further, more particularly, how the elastic properties of the W-X alloys are changing. According to Miedema et al. and Li and Wu, (see references [33,34]), for pure alkali metals and non-transition metals, $\sqrt{B/V_m}$ is linearly proportional to the electron density at the boundary of the Wigner-Seitz cell, where B is the bulk modulus and V_m is the molar volume of the element. The electron density at the boundary of the Wigner-Seitz cell, n , can be calculated via $n = Z_B / V$, where Z_B is the bond valence of the element and V is the atomic equilibrium volume at 0 K. This linear relationship has been validated for Ni-based alloys by taking into account the effect of alloying elements on n [8]. Here, in a similar manner, we compute n for $W_{53}X$ based on a linear combination of the constituent elements, similar to Vegard's law,

$$\text{Equation 16} \quad n_{W_{53}X} = \left(\frac{53}{54} n_W V_W + \frac{1}{54} n_X V_X \right) / V_{W_{53}X}$$

where the electron densities, n_W and n_X , are calculated from equilibrium volume[5] and bond valence data[34] of the pure elements found in published literature. Figure 6 shows that a linear relationship between $\sqrt{B/V_m}$ and electron density n is obeyed in dilute W-based alloys. It is found that the bulk modulus of $W_{53}X$ is positively proportional to the electron density, $n_{W_{53}X}$. In fact, the value of n reflects how dense the electron gas of a metallic system is. This is because

the bond valence (Z_B) is defined as the number of participating electrons where each atom contributes to the electron gas[35]. Thus, a higher electron density n indicates a denser electron gas, implying stiffer chemical bonds between the atoms[36]. Therefore, the $W_{53}X$ alloys with a higher electron density, n , are anticipated to have stiffer chemical bonds between atoms, which, in turn, would result in a larger bulk modulus.

The influence of alloying elements on the shear modulus along the $[111]$ direction of W can be better understood in terms of the differential charge densities that can be represented by the charge density difference for the calculated structure with and without the self-consistent calculations. Figure 7a, 7b, 7c, and 7d show the differential charge density plots in the $(1\bar{1}0)$ -plane of $W_{53}X$ (with $X=W, Mo, Ti,$ and Pd) revealing the bonding environments between nearest neighbors. The relative intensity and directionality of the differential charge density are illustrated by a combination of color mapping and contour plotting. As seen from Figure 7a, the charge density of pure W is higher between adjacent atoms in the $(1\bar{1}0)$ plane along the $\langle 111 \rangle$ directions; note, this distance (dashed arrow in Figure 7a) is the shortest distance between two W atoms. This implies that the interatomic bonds along the $\langle 111 \rangle$ directions in pure W are stronger than any other directions. As a result, the shear modulus along the $\langle 111 \rangle$ directions are expected to be larger than that associated with a polycrystalline microstructure (Table 1). Instead, from a polycrystalline microstructure, an average of shear moduli sampled from all directions would be expected. Furthermore, as seen from Figure 7c and 7d, the W-X bonds for W-Ti and W-Pd along the $\langle 111 \rangle$ directions are distorted and weaker than the W-W bonds. Correspondingly, the shear moduli G_{111} of $W_{53}Ti$ and $W_{53}Pd$ are much lower than that of pure W (Table 1). By analogy, the change of G_{111} caused by the alloying element Mo is relatively small; this can be attributed to the

fact that W-Mo bonds are very similar in nature to W-W type bonds (Figure 7b). Note, the crystal structures of Mo and W are isomorphous and they have similar atomic radii.

The observed decrease of the elastic shear moduli can be interpreted as a form of lattice softening induced by the alloying elements. Usually, it is considered that lattice softened alloys would lead to and may exhibit good plasticity due to the change of elasticity and crystal stability [23,37,38]. For example, the ideal shear strength in BCC crystals is governed by the shear modulus along the $\langle 111 \rangle$ directions, G_{111} [23]. As G_{111} decreases, the crystal lattice is expected to be softer or more deformable in response to a shear stress. Based on the Peierls-Nabarro model, the size of the dislocation glide barrier is also proportional to the shear modulus along the Burger's vector [39]. This implies that the glide of a $\frac{1}{2}\langle 111 \rangle$ screw dislocation in BCC W could be promoted as the G_{111} decreases. Therefore, it is conceivable that the lattice softening induced by alloying elements may also result in a preferential softening for plastic deformation in a practical sense as well. Experimentally, Re has been recognized to strongly soften BCC W at room temperature, however, with alloying contents of over 5 at.% [3,4,40]. In addition to Re, Ru, Os, or Ir have been reported to also have obvious softening effects on BCC W, but at much lower alloying levels (1~2 at.%) [3]. It is interesting to note that at very a low alloying concentration (1.85 at.%), the effect of Re on lattice softening (i.e., a decrease of G_{111}) is weaker compared to the effects of Ru, Os and Ir, as shown by the present calculations (Table 1). However, the lattice softening induced by Re becomes much more significant as at concentrations greater than 5 at.% [13]. As mentioned above, the alloying elements that have large disparities of the number of valence electrons compared to pure W will lead to significant decrease of G_{111} . Therefore, by taking the real solubility limits of alloy elements in BCC W into account, it is hypothesized that Ti, Rh, and Hf could be possibly more promising candidates to soften BCC W via alloying.

Nevertheless, it needs to be pointed out that this hypothesis is purely based on the elastic properties of the host metal and alloying additions which may not be able to reflect the overall effects of alloying on plasticity. Further experiments or calculations incorporating a better plasticity model are needed to validate the current hypothesis.

3.2 Elastic Properties at Finite Temperatures

The elastic properties of pure W and $W_{53}X$ type alloys at finite temperatures are predicted via the quasi-static approach based on the Debye model presented in Section 2.2. The Debye temperature of pure W is calculated to be 363 K in the present work, which is in good agreement with the experimental value (378 K) and results of a previous calculation (366 K) [6]. Figure 8 plots the predicted isentropic and isothermal c_{ij} 's and the bulk modulus of pure W from 0 to 3750 K. Available experimental data, measured in the isentropic condition, are also included for comparison [22,28,41]. It is shown that the predicted elastic constant values decrease with increasing temperature. This is caused by lattice expansion at high temperatures which leads to the weakening of atomic bonds. Computed values of the isothermal bulk modulus and c_{44} agree more closely with the experimental data. A relatively large discrepancy is observed between experimental c_{11} and the predicted values at high temperatures. This is possibly due to the strong anharmonicity in W at high temperatures or caused by the thermal stress fluctuations, which are not considered in the present work.

Table 2 summarizes the predicted isothermal and isentropic elastic constants of $W_{53}X$ at several selected temperatures, 300, 900, 1500, 2100, 2700, and 3300 K. It is worth mentioning that the value for the isothermal c_{44} equals to the isentropic c_{44} for a cubic crystal. Similarly to pure W, the predicted c_{ij} values of $W_{53}X$ decrease with increasing temperature. For the sake of

applicability, the predicted c_{ij} values of $W_{53}X$ from 300 to 3750 K are fitted to a polynomial function [11],

$$\text{Equation 17} \quad c_{ij}(T) = a_0 + a_1T + a_2T^2$$

where a_0 , a_1 , and a_2 are fitting parameters. The fitting parameters obtained for each $W_{53}X$ are listed in Table 2. In addition, fitting errors are estimated by,

$$\text{Equation 18} \quad \text{Error} = \sqrt{\frac{\sum [(c_{fit} - c_{calc}) / c_{calc}]^2}{n}}$$

where c_{calc} and c_{fit} are elastic stiffness constants predicted by the quasi-static approach and by Equation 17, respectively. These fitting errors are also included in Table 2. As seen in Table 2, the decreasing trend of elastic constants is indicated by a_1 roughly. The average values of a_1 for isothermal c_{11} , c_{12} and c_{44} are -2.88×10^{-2} , -1.60×10^{-2} and -0.58×10^{-2} GPa/K, respectively. For isentropic c_{11} and c_{12} , the average values of a_1 are -1.65×10^{-2} and -0.56×10^{-2} , respectively.

4. Conclusions

In the present work, the effects of alloying elements and temperature on the elastic properties of BCC W, including isothermal and isentropic elastic stiffness constants, bulk modulus, shear modulus, Young's modulus and elastic anisotropy have been studied systematically via first-principles calculations. Nineteen transition metal alloying elements (X's) have been considered: Ti, V, Cr, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, Re, Os, Ir, and Pt. Based on the first-principles results at 0 K, the alloying effects on the elasticity of BCC W can be summarized as follows: (i) the bulk modulus of the dilute W-X alloys decreases with increasing equilibrium volume, particularly for alloying elements in the same period; (ii) all alloying elements decrease

the shear modulus of BCC W to some extent; (iii) the earlier or later transition elements (e.g., Y, Zr and Pd) have stronger effects on the shear modulus than the other elements (e.g., Cr and Mo) which have the same number of valence electrons as W; and (iv) the largest decrease of elastic properties of W is due to the alloying element of Y. In addition, effects of alloying elements on the elastic properties of W, such as the bulk modulus and shear modulus, are traceable from the redistribution of electronic charge densities caused by alloying elements. At finite temperatures, the isothermal and isentropic elastic stiffness components of the W-X dilute alloys are predicted via a quasi-static approach based on the Debye model and show a decreasing trend of elasticity with increasing temperature due to lattice expansion at finite temperatures. Computed elastic properties are compared to available experimental data and are found to be in good agreement.

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Table 1. Calculated elastic properties of $W_{53}X$ alloys at 0 K, including elastic stiffness constants (c_{ij} 's), Young's modulus (E), bulk modulus (B), and shear modulus (G) from the Voigt approach, shear modulus along the [111] direction (G_{111}), and the universal elastic anisotropy ratio (A^U). The unit for each elastic property is GPa. The EOS predicted equilibrium volume (V_0 ($\text{\AA}^3/\text{atom}$)), the corresponding lattice parameter (a_0 ($\text{\AA}$)), and lattice regression coefficient (k_x) are shown as well. For BCC W, available experimental data and previous calculations are also included for comparison.

X	V_0	a_0	k_x	c_{11}	c_{12}	c_{44}	E	B	G	G_{111}	A^U
W	16.226	3.190	0.000	525.6	192.8	143.3	392.0	303.7	152.5	157.9	0.027
	16.229[5]	3.190		517.8	201.7	139.4					
Expt.[28]	15.856	3.165	0.000	533.9	205.1	163.3	418.6	314.7	163.7	164.0	0.000
Ti	16.206	3.188	-0.070	507.3	195.7	128.7	362.4	299.5	139.6	145.6	0.044
V	16.183	3.187	-0.154	515.6	193.7	136.1	377.1	301.0	146.0	151.7	0.034
Cr	16.160	3.185	-0.235	521.8	191.9	142.4	389.2	301.9	151.4	156.7	0.026
Fe	16.149	3.185	-0.271	503.2	203.4	135.7	367.1	303.3	141.4	144.8	0.012
Co	16.150	3.185	-0.268	499.0	202.3	135.3	364.9	301.2	140.5	143.7	0.010
Ni	16.160	3.185	-0.233	498.7	205.1	136.4	365.3	302.9	140.6	143.2	0.006
Y	16.346	3.198	0.423	495.8	191.2	128.9	358.3	292.7	138.2	143.6	0.034
Zr	16.300	3.195	0.263	493.4	197.3	126.1	351.3	296.0	134.9	139.9	0.031
Nb	16.255	3.192	0.103	517.2	192.9	138.7	381.6	301.0	148.1	153.5	0.029
Mo	16.220	3.189	-0.020	523.4	192.4	141.9	389.1	302.7	151.3	156.8	0.029

Ru	16.190	3.187	-0.126	505.2	201.5	136.9	370.4	302.7	142.9	146.5	0.013
Rh	16.209	3.189	-0.062	497.2	203.6	135.0	363.1	301.5	139.7	142.6	0.008
Pd	16.222	3.189	-0.015	491.5	205.4	135.0	359.7	300.8	138.3	140.3	0.004
Hf	16.285	3.194	0.208	505.8	194.5	130.4	364.2	298.3	140.5	146.2	0.038
Ta	16.254	3.192	0.098	517.2	193.9	138.6	381.2	301.7	147.8	153.1	0.028
Re	16.204	3.188	-0.079	523.4	195.2	143.2	390.0	304.6	151.6	156.5	0.022
Os	16.193	3.188	-0.118	512.8	201.2	142.7	382.1	305.1	147.9	151.2	0.009
Ir	16.201	3.188	-0.088	501.8	204.9	139.1	370.5	303.9	142.8	145.2	0.005
Pt	16.224	3.190	-0.009	492.6	206.1	138.3	364.4	301.6	140.3	141.6	0.001

Table 2. Predicted isothermal elastic stiffness constant (c_{ij}^T) and isentropic elastic stiffness constant (c_{ij}^S) of $W_{53}X$ at 300, 900, 1500, 2100, 2700, and 3300 K. The unit for the elastic stiffness constants is GPa. The polynomial fitting parameters and fitting errors are also included; their values are based on the predicted elastic data from 300 to 3300 K.

X	c_{ij}	T_{300}	T_{900}	T_{1500}	T_{2100}	T_{2700}	T_{3300}	a_0	$a_1 \times 10^2$	$a_2 \times 10^6$	$error \times 10^4$
W	c_{11}^T	516.9	500.0	482.2	463.6	444.1	423.2	524.7	-2.62	-1.40	4.1
	c_{12}^T	186.4	175.6	164.9	154.5	144.3	134.5	192.2	-1.88	0.40	4.6
	c_{44}^T	141.1	136.7	131.9	126.7	121.0	114.7	142.9	-0.62	-0.70	7.8
	c_{11}^S	519.5	508.0	495.0	480.8	465.4	448.7	525.1	-1.75	-1.72	1.9
	c_{12}^S	189.0	183.6	177.6	171.6	165.7	160.0	192.5	-1.01	0.08	11.2
	c_{44}^S	141.1	136.7	131.9	126.7	121.0	114.7	142.9	-0.62	-0.70	7.8
Ti	c_{11}^T	497.5	479.6	461.0	442.0	422.4	401.7	506.0	-2.85	-0.95	3.2
	c_{12}^T	190.0	179.1	168.3	157.3	146.2	134.9	195.1	-1.76	-0.20	5.3
	c_{44}^T	126.2	121.7	117.0	112.2	107.2	101.9	128.3	-0.71	-0.26	6.6
	c_{11}^S	500.4	488.5	475.2	461.1	446.2	430.2	506.3	-1.87	-1.33	2.2
	c_{12}^S	192.7	188.1	182.5	176.4	170.1	163.4	195.5	-0.78	-0.58	10.0
	c_{44}^S	126.2	121.7	117.0	112.2	107.2	101.9	128.3	-0.71	-0.26	6.6
V	c_{11}^T	505.8	487.6	468.9	449.8	430.1	409.7	514.6	-2.92	-0.76	3.6
	c_{12}^T	188.3	178.5	168.4	158.3	147.9	137.2	193.2	-1.61	-0.28	8.8
	c_{44}^T	133.5	128.5	123.4	118.1	112.7	107.0	135.9	-0.80	-0.24	7.4
	c_{11}^S	508.5	495.9	482.2	467.7	452.5	436.3	514.6	-1.97	-1.22	1.7
	c_{12}^S	191.0	186.8	181.8	176.2	170.3	163.8	193.2	-0.65	-0.74	5.4
	c_{44}^S	133.5	128.5	123.4	118.1	112.7	107.0	135.9	-0.80	-0.24	7.4
Cr	c_{11}^T	512.8	495.6	477.4	458.4	438.3	416.8	520.7	-2.64	-1.55	3.0
	c_{12}^T	186.0	175.4	164.7	154.0	143.5	132.9	191.4	-1.79	-0.04	6.2
	c_{44}^T	140.6	136.3	131.5	126.1	120.2	113.4	142.3	-0.58	-0.91	9.5
	c_{11}^S	515.6	504.3	491.4	477.1	461.5	444.8	521.3	-1.73	-1.77	3.5
	c_{12}^S	188.8	184.1	178.7	172.8	166.6	160.9	192.1	-0.88	-0.18	18.8
	c_{44}^S	140.6	136.3	131.5	126.1	120.2	113.4	142.3	-0.58	-0.91	9.5
Fe	c_{11}^T	496.8	480.1	462.2	443.6	423.8	402.7	504.7	-2.59	-1.51	2.5
	c_{12}^T	193.1	182.2	171.2	160.3	149.4	138.7	198.8	-1.86	-0.10	7.7
	c_{44}^T	135.2	131.1	126.5	121.4	115.7	109.2	136.8	-0.55	-0.87	6.1
	c_{11}^S	499.6	488.6	476.0	462.2	447.2	430.3	504.5	-1.58	-2.05	4.1
	c_{12}^S	195.9	190.8	185.0	178.9	172.8	166.3	198.6	-0.84	-0.43	5.9
	c_{44}^S	135.2	131.1	126.5	121.4	115.7	109.2	136.8	-0.55	-0.87	6.1

Co	c_{11}^T	488.9	470.4	451.5	432.6	413.7	394.6	498.4	-3.10	-0.13	2.4
	c_{12}^T	195.8	184.6	173.2	161.9	150.7	139.5	201.7	-1.91	0.08	4.1
	c_{44}^T	132.9	128.0	123.0	117.8	112.4	106.6	135.2	-0.76	-0.31	7.8
	c_{11}^S	491.7	479.1	465.6	451.5	437.3	422.8	498.6	-2.13	-0.51	4.2
	c_{12}^S	198.6	193.3	187.3	180.8	174.3	167.8	201.9	-0.94	-0.30	11.3
	c_{44}^S	134.0	129.2	124.1	118.8	113.1	107.0	136.1	-0.73	-0.47	8.5
Ni	c_{11}^T	489.0	470.8	452.0	432.7	412.9	392.4	497.9	-2.94	-0.78	0.8
	c_{12}^T	199.0	187.7	176.2	164.7	153.1	141.5	204.8	-1.90	-0.06	3.4
	c_{44}^T	134.0	129.2	124.1	118.8	113.1	107.0	136.1	-0.73	-0.47	8.5
	c_{11}^S	491.8	479.6	466.0	451.6	436.2	419.8	497.9	-1.92	-1.34	2.7
	c_{12}^S	201.9	196.5	190.3	183.6	176.4	169.0	204.9	-0.88	-0.62	8.6
	c_{44}^S	125.8	120.0	114.2	108.3	102.2	96.1	128.6	-0.94	-0.13	4.3
Y	c_{11}^T	485.5	465.9	445.9	425.6	405.0	383.9	495.1	-3.20	-0.52	1.2
	c_{12}^T	185.8	176.1	166.1	156.0	145.4	134.5	190.5	-1.55	-0.43	8.0
	c_{44}^T	125.8	120.0	114.2	108.3	102.2	96.1	128.6	-0.94	-0.13	4.3
	c_{11}^S	488.3	474.5	459.5	444.0	428.0	411.0	495.2	-2.22	-1.00	2.6
	c_{12}^S	188.6	184.7	179.8	174.3	168.4	161.6	190.6	-0.58	-0.92	7.2
	c_{44}^S	124.4	120.5	116.5	112.3	107.9	103.1	126.0	-0.58	-0.33	9.3
Zr	c_{11}^T	484.9	468.6	451.5	433.7	414.7	394.0	491.9	-2.43	-1.64	6.0
	c_{12}^T	191.7	181.1	170.5	160.2	150.0	139.8	197.0	-1.78	0.13	5.3
	c_{44}^T	124.4	120.5	116.5	112.3	107.9	103.1	126.0	-0.58	-0.33	9.3
	c_{11}^S	487.6	476.9	464.6	451.1	436.4	420.5	493.0	-1.65	-1.66	2.9
	c_{12}^S	194.4	189.3	183.6	177.6	171.7	166.3	198.1	-1.00	-0.12	17.4
	c_{44}^S	136.3	130.9	125.3	119.7	113.8	107.6	138.9	-0.86	-0.26	5.3
Nb	c_{11}^T	508.5	490.7	472.2	453.2	433.4	412.7	517.0	-2.83	-1.01	2.2
	c_{12}^T	187.1	177.1	167.0	156.9	146.7	136.5	192.2	-1.68	-0.03	4.8
	c_{44}^T	136.3	130.9	125.3	119.7	113.8	107.6	138.9	-0.86	-0.26	5.3
	c_{11}^S	511.1	498.9	485.3	470.7	455.3	438.3	516.8	-1.86	-1.59	3.5
	c_{12}^S	189.8	185.3	180.0	174.4	168.6	162.1	192.1	-0.71	-0.61	5.4
	c_{44}^S	140.0	135.7	131.1	126.0	120.4	114.0	141.7	-0.59	-0.76	7.8
Mo	c_{11}^T	515.0	498.8	481.4	463.0	443.3	421.9	522.2	-2.43	-1.85	3.2
	c_{12}^T	186.4	175.7	165.0	154.4	143.9	133.6	192.0	-1.83	0.18	3.3
	c_{44}^T	140.0	135.7	131.1	126.0	120.4	114.0	141.7	-0.59	-0.76	7.8
	c_{11}^S	517.7	507.1	494.8	481.0	465.8	448.4	522.1	-1.45	-2.38	3.1
	c_{12}^S	189.1	184.0	178.3	172.4	166.4	160.0	191.9	-0.85	-0.35	5.7
	c_{44}^S	134.1	128.8	123.3	117.8	112.1	106.2	136.7	-0.86	-0.19	3.1
Ru	c_{11}^T	495.2	476.9	458.0	438.7	419.0	398.6	504.2	-2.98	-0.69	4.1
	c_{12}^T	195.7	185.2	174.4	163.5	152.4	141.2	201.0	-1.75	-0.21	10.3
	c_{44}^T	134.1	128.8	123.3	117.8	112.1	106.2	136.7	-0.86	-0.19	3.1

Rh	c_{11}^S	498.0	485.6	472.0	457.7	442.7	426.9	504.5	-2.01	-1.04	3.2
	c_{12}^S	198.5	193.9	188.4	182.4	176.1	169.6	201.3	-0.78	-0.56	9.4
	c_{11}^T	488.4	471.4	453.6	435.3	416.1	395.8	496.4	-2.67	-1.15	2.5
	c_{12}^T	197.6	186.7	175.6	164.5	153.5	142.4	203.2	-1.84	0.03	14.3
Pd	c_{44}^T	133.0	129.1	124.8	119.9	114.4	108.1	134.6	-0.52	-0.85	6.3
	c_{11}^S	491.1	480.0	467.4	453.8	439.2	423.1	496.4	-1.67	-1.66	3.1
	c_{12}^S	200.4	195.2	189.4	183.1	176.6	169.8	203.2	-0.85	-0.51	7.1
	c_{11}^T	481.8	463.4	444.4	425.2	405.6	385.5	491.0	-3.02	-0.54	1.4
Hf	c_{12}^T	199.4	188.4	177.2	165.8	154.4	142.9	205.0	-1.84	-0.14	6.1
	c_{44}^T	132.6	127.8	122.7	117.4	111.9	106.1	134.9	-0.77	-0.32	7.5
	c_{11}^S	484.6	472.3	458.7	444.4	429.5	414.2	491.3	-2.05	-0.88	4.6
	c_{12}^S	202.3	197.3	191.4	185.1	178.4	171.6	205.4	-0.86	-0.48	12.8
Ta	c_{11}^T	496.1	478.3	460.0	441.3	422.1	402.0	504.6	-2.84	-0.83	3.1
	c_{12}^T	188.9	178.5	168.0	157.5	146.9	136.1	194.0	-1.71	-0.12	5.8
	c_{44}^T	127.4	122.3	117.1	111.8	106.6	101.2	130.0	-0.85	-0.07	3.2
	c_{11}^S	498.8	486.7	473.3	459.2	444.4	428.7	505.1	-1.96	-1.08	3.0
Re	c_{12}^S	191.6	186.9	181.3	175.4	169.2	162.8	194.6	-0.83	-0.38	13.6
	c_{11}^T	508.2	491.0	473.1	454.5	434.9	414.2	516.1	-2.66	-1.30	2.6
	c_{12}^T	188.2	177.7	167.1	156.7	146.2	135.8	193.5	-1.76	-0.05	7.1
	c_{44}^T	136.2	131.6	126.7	121.4	115.6	109.1	138.1	-0.65	-0.68	8.2
Os	c_{11}^S	510.9	499.4	486.4	472.4	457.2	440.9	516.6	-1.78	-1.56	2.0
	c_{12}^S	190.8	186.0	180.4	174.5	168.5	162.5	194.0	-0.88	-0.22	12.6
	c_{11}^T	513.7	496.0	477.4	458.2	438.0	416.8	522.2	-2.79	-1.23	2.1
	c_{12}^T	189.2	178.2	167.0	155.9	145.0	134.1	195.0	-1.88	-0.09	6.8
Ir	c_{44}^T	140.3	134.9	129.2	123.5	117.6	111.6	143.0	-0.89	-0.18	4.0
	c_{11}^S	516.6	504.8	491.6	477.3	461.8	445.5	522.5	-1.84	-1.50	2.4
	c_{12}^S	192.0	186.9	181.2	175.1	168.8	162.7	195.3	-0.93	-0.18	12.8
	c_{11}^T	501.5	477.8	454.7	432.6	411.7	392.2	514.6	-4.24	1.61	4.7
Ir	c_{12}^T	195.8	185.1	174.2	163.2	152.2	141.1	201.3	-1.79	-0.10	3.5
	c_{44}^T	138.7	132.0	125.3	118.8	112.6	106.6	142.4	-1.19	0.31	6.9
	c_{11}^S	504.3	486.7	468.7	451.3	434.9	419.7	514.8	-3.26	1.15	7.9
	c_{12}^S	198.7	193.9	188.2	182.0	175.4	168.6	201.6	-0.81	-0.57	9.9
Ir	c_{11}^T	491.6	473.2	454.1	434.6	414.5	393.7	500.5	-2.96	-0.85	2.1

Pt	c_{12}^T	199.2	188.7	178.0	167.2	156.4	145.5	204.5	-1.75	-0.13	5.6
	c_{44}^T	135.8	130.3	124.5	118.5	112.2	105.7	138.5	-0.88	-0.34	3.5
	c_{11}^S	494.3	481.7	467.9	453.1	437.5	421.2	500.8	-2.03	-1.15	3.2
	c_{12}^S	201.9	197.2	191.7	185.7	179.4	173.0	204.8	-0.82	-0.44	9.7
	c_{11}^T	482.9	464.8	446.2	427.1	407.6	387.4	491.7	-2.92	-0.72	1.7
	c_{12}^T	200.3	189.7	178.9	167.9	156.7	145.3	205.6	-1.75	-0.25	8.1
	c_{44}^T	135.5	130.2	124.7	119.1	113.4	107.5	138.1	-0.86	-0.20	3.1
	c_{11}^S	485.6	473.5	460.2	446.1	431.3	415.9	492.0	-1.97	-1.01	3.8
	c_{12}^S	203.1	198.4	192.9	186.8	180.4	173.8	205.9	-0.80	-0.54	10.0

Figure 1. Calculated equilibrium volumes of the $W_{53}X$ alloys (listed in Table 1) compared to the predictions from Vegard's law of pure elements with a BCC structure [5]. The dashed line indicates where the two methods produce the same result.

Figure 2. Calculated lattice regression coefficients (k_x) of the $W_{53}X$ alloys (see Equation 15) vs. lattice parameters of the alloying elements (Xs) in the BCC structure [5]. The k_x values fitted from experimental data are labeled as black dots [31,32].

Figure 3. Bulk modulus of the $W_{53}X$ alloys (listed in Table 1) compared to the predictions from a linear combination of bulk moduli of the pure elements in the BCC structure in terms of their mole fractions [5]. The dashed line indicates where the two methods agree.

Figure 4. Calculated bulk and shear moduli of the $W_{53}X$ alloys based on the Voigt approach as a function of the equilibrium volume; (a) bulk modulus and (b) shear modulus.

Figure 5. Calculated shear moduli of the $W_{53}X$ alloys with respect to the number of the valence electrons of the alloying elements.

Figure 6. Correlation between n and $\sqrt{B/V_m}$ for the $W_{53}X$ alloys.

Figure 7. Differential charge densities of pure BCC W and the $W_{53}X$ alloys in the $(1\bar{1}0)$ plane; (a) pure BCC W, (b) $W_{53}\text{Mo}$, (c) $W_{53}\text{Ti}$, and (d) $W_{53}\text{Pd}$. The shortest distance between two W atoms or the solute and W atom is shown by dashed arrows. Note, the lattice indices in the figures are with respect to the 54-atom supercell. The unit of charge density is $e/\text{\AA}^3$. Contour lines are spaced at $0.002 e/\text{\AA}^3$.

Figure 8. Predicted isentropic and isothermal c_{ij} values of pure W from 0 to 3750 K. Available experimental data are also included for comparison ($\square$ [28], $\circ$ [22], Δ [41])

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