The First-Principles Design of Ductile Refractory Alloys

Michael C. Gao, Ömer N. Doğan, Paul King, Anthony D. Rollett, and Michael Widom

The purpose of this work is to predict elastic and thermodynamic properties of chromium-based alloys based on first-principles calculations and to demonstrate an appropriate computational approach to develop new materials for high-temperature applications in energy systems. In this study, Poisson ratio is used as a screening parameter to identify ductilizing additives to the refractory alloys. The results predict that elements such as Ti, V, Zr, Nb, Hf, and Ta show potential as ductilizers in Cr while Al, Ge, and Ga are predicted to decrease the ductility of Cr. Experimental evidence, where available, validates these predictions.

INTRODUCTION

In order to reduce environmental emissions in fossil power generation, more efficient energy-generating technologies such as oxy-fuel gas turbines, hydrogen turbines, and syngas turbines are being developed. One common barrier in the development of these different technologies for future energy generating systems is an insufficiency of existing materials at high temperatures (>1,150ºC) and aggressive atmospheres (e.g., steam, oxygen, CO_2). Even the highly alloyed and costly nickel-based superalloys do not have the desired properties for these applications since they soften at ~1,100ºC. To enable the development of these new technologies, new materials with high strength, good ductility and fracture toughness, and resistance against creep, high-temperature corrosion, wear, and thermal fatigue have been sought.

Alloys of body-centered cubic (bcc) refractory metals with high melting points[1,2] are promising candidate materials for these structural applications. For example, the melting points (T_m) of chromium, niobium, and molybdenum are 1,863ºC, 2,469ºC, and 2,623ºC, respectively. In particular, chromium alloys are attractive because they have low density, high thermal conductivity, and high strength at elevated temperatures. Chromium generally forms a dense surface scale of Cr_2O_3 that possesses excellent corrosion resistance at high temperatures (≤900–1,100ºC depending on oxygen partial pressure). In addition, strategies have been developed for the chromium alloys to maintain acceptable oxidation resistance at elevated temperatures (≥1,000ºC).[3] More importantly, chromium is inexpensive compared to the other refractory metals because it is more abundant. However, its low-temperature (e.g., at room temperature) brittleness and embrittlement from nitrogen contamination at elevated temperatures have prevented it from major engineering applications.[4] ("Low temperature" in this report refers to low homologous temperature [e.g., <0.3T_m]). In fact, the lack of low-temperature ductility (e.g., high ductile-to-brittle transition temperature [DBTT]) is a common weakness of some refractory metals, such as chromium, molybdenum and tungsten, and their alloys.[5] Therefore, studying how to improve the ductility of refractory metal alloys is important and yet challenging.

There are two main difficulties in developing refractory alloys: first, a lack of basic experimental data on the thermodynamics and mechanical and physical properties of most of these alloy systems, and second, difficulties associated with processing of these alloys. In order to avoid traditional trial-and-error experiments that are also time consuming and expensive, it has become essential to develop theoretical modeling to guide experimental alloy development. Such theoretical modeling can be multiscale in nature, which includes first-principles density functional theory (DFT) calculations, and atomistic, mesoscale, and continuum simulations. Due to their interpretative and predictive capacities, first-principles calculations are widely employed to study alloy lattice stability, interfacial energies, defect structures, etc.[6–16] This report presents first-principles calculations on a series of chromium-based binary alloys for initial screening

How would you . . .

describe the overall significance of this paper?

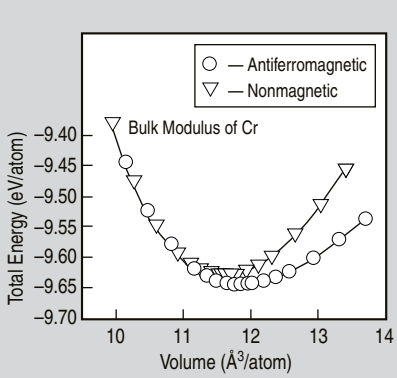
This paper describes an alloying strategy to improve intrinsic ductility of chromium-based alloys at low temperatures using first-principles density functional theory calculations. Experimental evidence, where available, validates the predictions made in this work.

describe this work to a materials science and engineering professional with no experience in your technical specialty?

This paper uses Poisson's ratio as the screening parameter to identify potential ductilizing additives to the refractory elements such as chromium. First-principles density functional theory calculations are used to predict Poisson's ratio of various chromium binary alloys. The results indicate that Poisson's ratio can be a good indicator of intrinsic ductility of metals and alloys.

describe this work to a layperson?

The goal of this work is to accelerate the design of new materials using quantum mechanical calculations. This work has identified several potentially powerful ductilizing elements to chromium.



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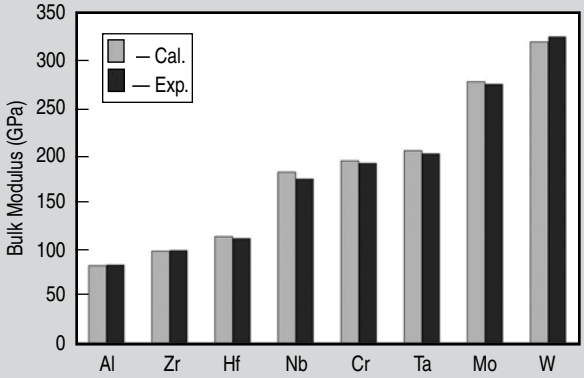

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Figure 1. (a) Total energy vs. volume for bcc chromium in antiferromagnetic and nonmagnetic states; (b) a comparison between calculated and experimental bulk modulus for selected pure elements.

of alloying elements to improve the intrinsic ductility of chromium.

It is well known that the Poisson ratio is well correlated with ductility of crystalline alloys[17,18] and amorphous metals.[19,20] The higher the Poisson ratio is, the better ductility the crystalline or amorphous metal has at low temperatures. For example, gold has a Poisson ratio of 0.42 and it has an elongation of 50%; niobium has a Poisson ratio of 0.40 and it has an elongation of 44% at room temperature. Other ductile metals (e.g., silver, palladium, and copper) also have high values of Poisson ratio. In contrast, commonly known brittle metals have low values of Poisson ratio. For example, beryllium has a Poisson ratio of 0.08 and its tensile elongation is only 1%; chromium has a Poisson ratio of 0.21 and it is very brittle below its DBTT, which is about 150ºC. Similar trends are also observed in wholly or partially amorphous metallic alloys.[19,20] Therefore, Poisson ratio is chosen as the first screening tool to gauge ductility in this project. Moreover, it can be evaluated completely from first-principles calculations with virtually no empirical information.

A survey of established chromium-based binary phase diagrams[21] indicates that feasible alloying elements are Ti, V, Fe, Co, Ni, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir, Pt, Al, Si, Ga, and Ge. These elements are soluble to varying extents in bcc chromium up to very high temperatures, whereas all other elements in the periodic table exhibit essentially negligible solubility. Therefore, all 22 elements were evaluated as potential substitutional alloying elements in this study. For comparison purposes, the elasticity of pure chromium with 6.25 at.% vacancies was also calculated.

COMPUTATIONAL DETAILS AND METHODOLOGY

The first-principles calculations use the plane-wave code VASP[22,23] which solves for the electronic band structure using electronic density functional theory. Projector augmented-wave[24] pseudopotentials are used as supplied with VASP. This study uses the Perdew-Burke–Ernzerhof[25] gradient approximation to the exchange-correlation functional.

Reciprocal space (k-point) meshes are increased to achieve convergence to a precision of better than 1 meV/at. All structures are fully relaxed (both lattice parameters and atomic coordinates) until energies converge to a precision of 0.25 meV/at. A "high precision" setting is used since the derivative of total energy is required for calculation of elastic properties. The plane-wave energy cutoff is held constant across each binary system at 500 eV.

The semi-core 3p, 4p, and 5p electrons of selected transition metals are explicitly treated as valence electrons. Spin polarization with collinear magnetization or anti-ferromagnetism is considered in all calculations since chromium is known to be anti-ferromagnetic at its ground state. To examine the substitutional effect, a 2×2×2 bcc supercell is built and then one chromium atom is replaced with one alloying element. Thus the alloy composition is fixed at $Cr_{15}X_1$ (X = 6.25 at.%) in the present study.

For a material with cubic symmetry, there are three independent single-crystal elastic constants: the bulk modulus $B = \frac{1}{3}\left(C_{11} + 2C_{12}\right)$, the tetragonal shear modulus $C' = \frac{1}{2}\left(C_{11} - C_{12}\right)$, and the trigonal shear modulus C_{44}. All three elastic constants must be positive in order for the structure to be mechanically stable. In the present study, we obtained these elastic constants using the approach proposed by M.J. Mehl et al.[6]

To obtain the equilibrium unit cell

Equations

$$B = -\left(V\frac{\partial P}{\partial V}\right)_{E_{min}} = V\left.\frac{\partial^2 E}{\partial V^2}\right|_{E_{min}} \quad (1)$$

$$\ddot{\varepsilon}_o = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \quad (2)$$

$$\Delta E(\delta) = \Delta E(-\delta) = E(0) - E(\delta) = (C_{11} - C_{12})V_0\delta^2 + O[\delta^4] \quad (3)$$

$$\ddot{\varepsilon}_m = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2/(4-\delta^2) \end{pmatrix} \quad (4)$$

$$\Delta E(\delta) = \Delta E(-\delta) = E(0) - E(\delta) = \tfrac{1}{2}C_{44}V_0\delta^2 + O[\delta^4] \quad (5)$$

$$G^3 + \frac{9B + 4C'}{8}G^2 - \frac{3C_{44}(B + 4C')}{8}G - \frac{3C_{44}C'B}{4} = 0 \quad (6)$$

$$\nu = \frac{3B - 2G}{6B + 2G} \quad (7)$$

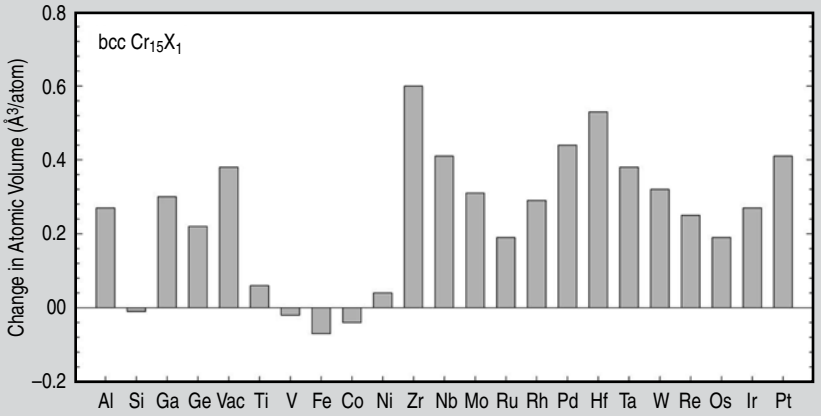

Figure 2. The effect of alloying elements on the atomic volume of bcc $Cr_{15}X_1$. The label "Vac" signifies monovacancy.

volume and bulk modulus, the total energies were calculated at 15 different volumes and then fitted to the basic equation of state while preserving the shape of bcc lattice (see Equation 1; all equations are shown in the table).

An example is shown in Figure 1a for chromium. It is found that the antiferromagnetism of chromium is critically important to predict correct physical properties of chromium. Thus, all calculations on $Cr_{15}X_1$ structures are initiated with an antiferromagnetic structure. To obtain the shear moduli C´ and C_{44}, the authors applied volume-conserving orthorhombic and monoclinic strains to the bcc lattice,[6] respectively, as shown in Equations 2–5.

The present study adopted A.V. Hershey's averaging method.[26] According to this method, the polycrystalline shear modulus is obtained by solving Equation 6.

Finally, for cubic materials, the Poisson ratio is calculated as Equation 7.

RESULTS AND DISCUSSIONS

Figure 1b shows the comparison between calculated bulk modulus and experimental values for selected pure elements. Clearly the agreement is excellent and the difference in all falls within 2.5%. This validates the calculation method.

The effect of alloying elements on the atomic volume and heat of mixing in the bcc structure of $Cr_{15}X_1$ is shown in Figures 2 and 3, respectively. Elements Si, V, Fe, and Co lower the average atomic volume when forming bcc $Cr_{15}X_1$ substitution solid solution while all other elements increase it. Calculations on the enthalpy of mixing in forming bcc $Cr_{15}X_1$ solid solution show that all the elements have a repulsive reaction with chromium in bcc lattice except Al, Si, and V. No correlation is found between atomic volume and enthalpy of mixing.

The effect of alloying elements on the bulk modulus and shear modulus in the bcc $Cr_{15}X_1$ is shown in Figures 4 and 5, respectively. Calculations predict that 11 elements plus the 6.25 at.% monovacancy lower the bulk modulus of Cr, including Al, Si, Ga, Ge, Ni, Zr, Nb, Rh, Pd, Hf, Pt, and Zr. In contrast, alloying with all 22 elements and vacancy lowers the shear modulus. The hexagonal close-packed (hcp) elements (Zr, Hf, and Ti) have a pronounced effect on the shear modulus of Cr; they lower it by 30 GPa, 25 GPa, and 19 GPa, respectively.

The effect of alloying elements on the Poisson ratio of bcc $Cr_{15}X_1$ is shown in Figure 6. All elements increase the Poisson ratio of Cr except Al, Ge, and Ga. Titanium increases it by 21%, followed by V, Ta, Zr, Hf, and Nb. It is worth noting that vacancy substitution increases the Poisson ratio by 25% because vacancy substitution lowers the shear modulus by 36 GPa (Figure 5).

Present theoretical calculations predict that all the transition metals selected tend to increase the Poisson ratio moderately for the 6.25 at.% compositions, thus improving the ductility of chromium. The results are supported by several experimental findings.[3,27–31] For example, our calculations predict that the Cr-6.25 at.%V alloy enhance the Poisson ratio of chromium by 15%, and H. Kurishita et al.[27] found that a properly processed V-52Cr-1.8Y (wt.%) alloy achieved a yield strength of 610–740 MPa and a total elongation of 10–19% at room temperature. This study predicts that a Cr-6.25 at.%Re alloy can increase the Poisson ratio of pure chromium by 10%, and it was reported that alloying of Re (≥20 at.%) to chromium can significantly improve the low-temperature ductility and fabricability of chromium.[28] Recently, M.P. Brady et al.[29] found that a eutectic microstructure that consists of an iron-rich bcc matrix and brittle strengthening Cr_2Ta intermetallics at a relatively large volume fraction (Cr-30Fe-6.3Ta-4Mo-0.5Ti-0.3Si-0.1La) exhibited a toughness of 20 MPa√m at room temperature and a yield strength of 350

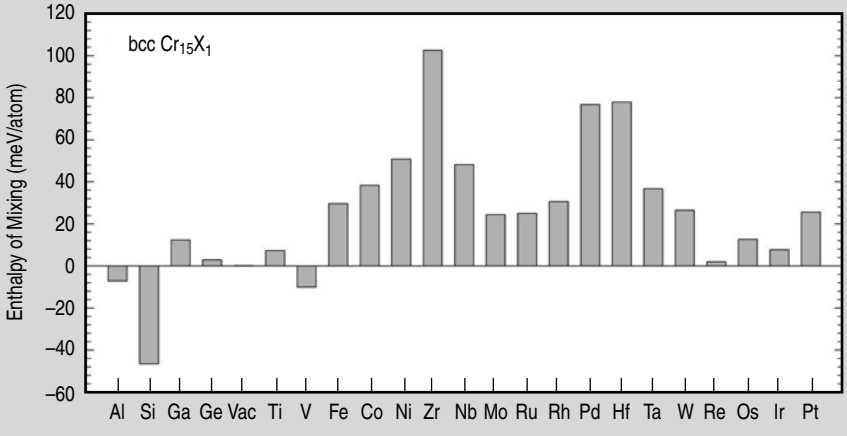

Figure 3. The effect of alloying elements on the heat of mixing of bcc $Cr_{15}X_1$.

MPa at 1,000ºC. The present study predicts that iron is a moderate ductilizer because the $Cr_{15}Fe_1$ alloy increases the Poisson ratio by 7%. The other advantages of choosing iron are that iron is very inexpensive, and that iron and chromium forms an extensive solid solution over a wide range of temperature and composition. In order to enhance the oxidation resistance by forming Al_2O_3 surface scale, alloying chromium with aluminum was practiced by several research groups,[3,30,31] but it was found that the addition of 5 at.% Al[30] or 10 at.%Al[3,31] deteriorates ductility significantly. This is in excellent agreement with the present prediction that shows the bcc $Cr_{15}Al_1$ alloy has a 7% lower Poisson ratio than pure chromium.

The present study also predicts that hcp metals (Ti, Zr, Hf) have a potent ductilizing effect. This agrees with another theoretical study[12] that used the Rice–Thompson parameter[32] as the ductility prediction parameter for molybdenum alloys. However, these hcp metals have low solubility in chromium, so alloying strategies to enhance their solubility in ternary and higher-order systems will be needed. Again, there is little information on phase diagrams for these systems, which motivates further theoretical calculations.

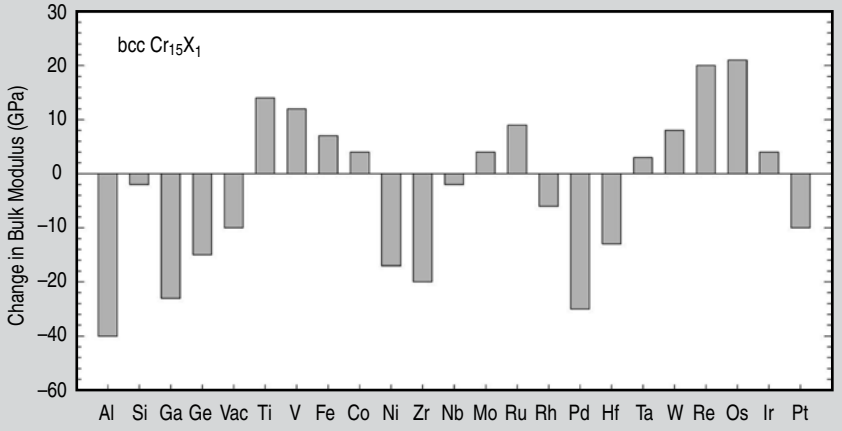

Figure 4. The effect of alloying elements on the bulk modulus of bcc $Cr_{15}X_1$.

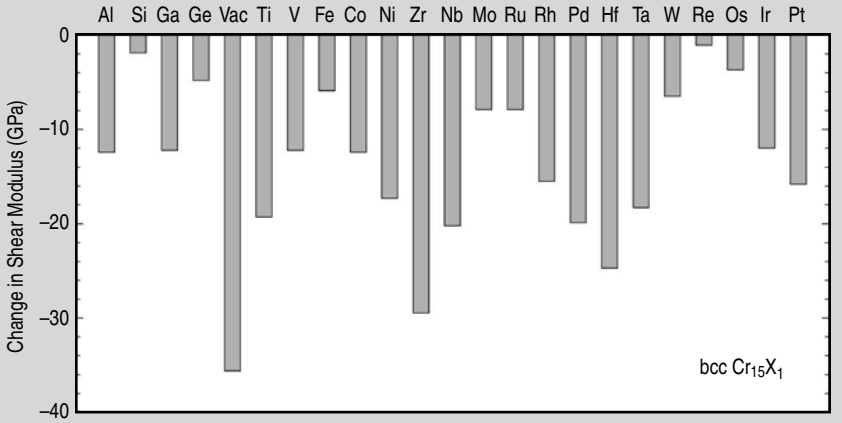

Figure 5. The effect of alloying elements on the shear modulus of bcc $Cr_{15}X_1$.

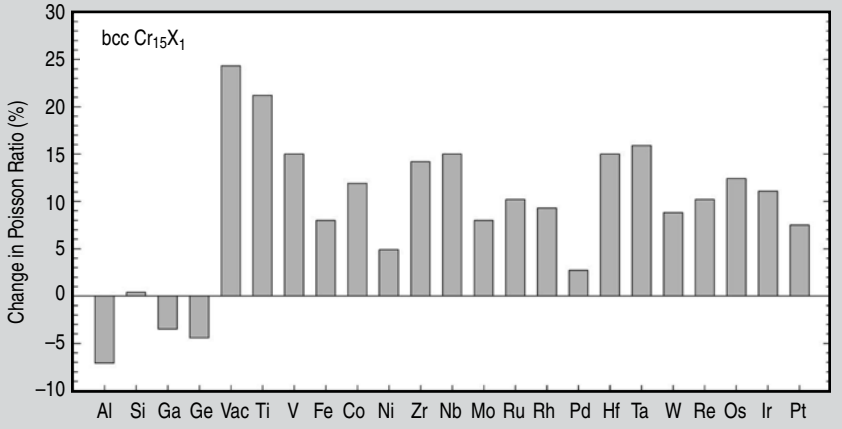

Figure 6. The effect of alloying elements on the Poisson ratio of bcc $Cr_{15}X_1$.

CONCLUSIONS

Based on the first-principles DFT calculations on the Poisson ratio of 22 bcc $Cr_{15}X_1$ alloys, one can conclude that on an atom-for-atom basis, Ti, V, Zr, Nb, Hf, and Ta are predicted to be potent ductilizers in chromium. Recent experiments by H. Kurishita et al.[27] demonstrated that alloying vanadium to chromium with proper processing improved the room-temperature ductility of chromium significantly. Rhenium and iron are predicted to be moderate ductilizers in chromium. There is experimental evidence for ductilization of chromium by rhenium and iron.[28,29] In addition, Al, Ge, and Ga are predicted to embrittle Cr. Again, there is experimental evidence that aluminum degrades the ductility of chromium.[3,30,31] Finally, the calculated elastic properties are found to be in good agreement with reported experiments, indicating that Poisson ratio can be used as a screening parameter for alloy development.

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