A lightweight single-phase AlTiVCr compositionally complex alloy

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Abstract:

A lightweight (5.06 g.cm⁻³) AlTiVCr compositionally complex alloy consisting of four elements is presented. Interest in the system is due to its microstructural uniformity and the use of commodity elements. The focus of the present work was to highlight the systematic microstructural and chemical characterization – and the information gained by application of various physical and modeling techniques in concert – in the context of complete characterization of compositionally complex alloys. Herein, analysis of as-cast AlTiVCr was investigated via conventional and scanning transmission electron microscopy, revealing a simple, single-phase microstructure. Characterization was supported by atom probe tomography and X-ray diffraction, whilst first-principles calculations based on density functional theory (DFT) were employed to calculate the thermodynamic and structural properties of the AlTiVCr alloy. The study was able to reveal the unique atomic locations in the alloy, whilst revealing that the B2 phase has a lower formation enthalpy (-9.30 kJ/mol atom) and is more stable than the disordered BCC phase (-1.25 kJ/mol atom) at low temperatures. The study herein provides insight into the combined analysis methods as relevant to the study of compositionally complex and high entropy alloys, indicating means of unambiguous characterization employing generalized multicomponent short range order analysis.

Keywords: compositionally complex alloy, high entropy alloy, transmission electron microscopy, atom probe tomography, X-ray diffraction, first-principles modeling

1. Introduction

Recent years have seen significant interest in so-called high entropy alloys (HEAs), which are defined as solid solution alloys that nominally contain five or more principal elements in equal or near-equal atomic percentage [1]. This rather rigid description has been shown to be difficult to achieve in a general sense, with HEAs exhibiting somewhat complex microstructures due to the formation of intermetallics [2], which also may contribute to low ductility and may make any processing difficult to undertake. Indeed for some HEAs [3-7], only a body-centered cubic (BCC), face-centered cubic (FCC), or in a few cases, hexagonal close packed (HCP) solid solution phase forms, free from secondary phases. Such alloys have reported to contribute to a range of interesting properties, such as high strength [8], high thermal stability [9] and high corrosion resistance [10].

To this end, a wider range of HEAs are being sought, and thus in order to expand the portfolio of such alloys, a number of issues are emerging. Firstly, the notion that alloys must have five or more principal elements in equal or near-equal atomic percentages to be termed an HEA is one aspect that can lead to alloys which violate the HEA nomenclature. Secondly, the notion of requiring 'high entropy' is also one aspect that if not required, may violate the HEA nomenclature. As a consequence, the more universal description of 'compositionally complex alloys' (CCAs) has emerged [11]. Nonetheless, it is of relevance to briefly review and describe the empirical concepts that have been used to date for HEAs, in the context of predicting elemental combinations that may result in a single (solid solution) phase [2,12-20]; whereby from empirical analysis the following parameters are normally taken into consideration: the entropy of mixing, ΔS_{mix} , the enthalpy of mixing, ΔH_{mix} , and the atomic size parameter, δ . According to Boltzmann's hypothesis, the mixing entropy of N-element regular solution alloys can be described by:

$$\Delta S_{mix} = -R \sum_i^n c_i \ln c_i \quad (1)$$

where R is the universal gas constant, and c_i is the molar content of the i^{th} component [2]. The enthalpy of mixing ΔH_{mix} may be given by:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n \Omega_{ij} c_i c_j \quad (2)$$

where $\Omega_{ij} = -4\Delta H_{AB}^{mix}$, c_i is the molar content of component, and ΔH_{AB}^{mix} is the mixing of enthalpy for binary system [2].

The so-called atomic size parameter δ can be determined as:

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (3)$$

where $\bar{r} = \sum_{i=1}^n c_i r_i$ is the average atomic radius, and r_i is the atomic radius of the i^{th} component.

It has been proposed that to form a solid solution, in the case of HEAs specifically, there should be a small atomic size difference, near-zero values of the (absolute) enthalpy of mixing, and a high entropy of mixing. To be more specific, it has been stated that the atomic size differences should be smaller than 6.5 %, the enthalpy of mixing should be in the range of -15 kJ mol^{-1} to 5 kJ mol^{-1} , and the entropy of mixing in the range of $12-17.5 \text{ J K}^{-1} \text{ mol}^{-1}$ [2]. Compared with the entropy of mixing, the enthalpy of mixing is obviously large, which is normally in kJ mol^{-1} , however, $T\Delta S_{mix}$ can compete with the enthalpy of mixing at high temperatures. In this vein, since (i) a high entropy of mixing can stabilize a solid solution phase at high temperature, and (ii) a negative enthalpy of mixing leads to the formation of intermetallic compounds, and (iii) a large positive enthalpy of mixing leads to elemental segregation, Yang and Zhang proposed a parameter, Ω , to estimate the solid solution formability [15]:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (4)$$

where T_m is the melting temperature of an n-element HEA, and was suggested to be estimated from the rule of mixtures,

$$T_m = \sum_{i=1}^n c_i (T_m)_i \quad (5)$$

where $(T_m)_i$ is the melting temperature of the i^{th} element, c_i is the atomic percentage of the i^{th} component.

$T\Delta S_{mix}$ can be regarded as the driving force to form a solid solution, whilst $|\Delta H_{mix}|$ is the solid solution formation resistance. When $\Omega \leq 1$, ΔH_{mix} dominates ΔS_{mix} with respect to free energy, and intermetallic compounds or segregation occurs. When $\Omega > 1$, so-called HEAs are more likely to be a solid solution. Such empirical rules have been a convenient set of descriptions, where it has been reported in the literature that when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$, simple solid solutions form [15, 21]. Furthermore, empirical work has also indicated that the valence electron concentration (VEC) influences whether a FCC or BCC phase is stable in a HEA [16], i.e. FCC is purported to be more stable with high VEC values, and BCC stable with low VEC values. However, such empirical rules are indeed simply empirical, and there are emerging demonstrations in the literature that indicate the inability to form a single-phase HEA alloy. However, in the present work we seek to explore the use of the above empirical rules in order to attempt to report their application to a four-component system, and to then contrast such rules to independent modeling using first principle calculations.

In terms of exploring compositionally complex alloys and their prospects, lightweight (i.e. low-density) structural materials with high specific properties are of key interest for subsequent energy efficiency. Several efforts have been made in this regard for alloys termed HEAs, for example Li *et al.* studied Mg-containing HEAs prepared by induction melting and casting [22, 23]. For $Mg_x(MnAlZnCu)_{100-x}$ [22], the density of these alloys varied from 4.29 g cm^{-3} to 2.20 g cm^{-3} depending on the atomic percentage of Mg ($x = 20, 33, 43, 45.6$ and 50

respectively). However these alloys had a multi-phase structure, mainly HCP phase and the Al-Mn icosahedral quasicrystal phase [24], and therefore not strictly HEAs, and also exhibited good compressive strength (400-500 MPa) at room temperature, with some ductility. Similar structures and properties were observed for the equi-atomic system, MgMnAlZnCu [23]. Chen *et al.* [25] prepared low-density BeCoMgTi and BeCoMgTiZn alloys by mechanical alloying, however in such instances, only amorphous phases were obtained. Also of interest, a series of Al-, Li- and Mg-based lightweight HEAs [26] were prepared by induction melting were studied with densities varying from 2.84 g cm^{-3} ($\text{Al}_{80}\text{Li}_5\text{Mg}_5\text{Zn}_5\text{Sn}_5$) to 3.88 g cm^{-3} (AlLiMgZnSn). Such alloys exhibited complex microstructures and consisted of numerous intermetallic phases – whilst the concept of equiatomic proportions also contributed to the alloys not strictly being HEAs. Recently, Youssef *et al.* developed a low density (2.67 g cm^{-3}) $\text{AlLiMg}_{0.5}\text{ScTi}_{1.5}$ alloy using mechanical alloying [7]. The authors called the alloy an HEA, however the composition may not be considered near-equiatomic, further highlighting the ambiguity that stems from the use of the term HEA. The $\text{AlLiMg}_{0.5}\text{ScTi}_{1.5}$ alloy formed a single phase FCC structure after preparation by ball milling, which transformed to a HCP structure after annealing at 500°C for 1 hour. Both the as-ball-milled and annealed conditions exhibited high hardness, 5.9 GPa and 4.9 GPa, respectively, but the upscaling, cost, and ease of production are all prohibitive. Nonetheless, based on the work reported to date, it is clear that further research is required to develop new lightweight compositionally complex alloys with desirable single-phase microstructures, which use low-cost elements and can be produced by conventional melt-based processes.

Utilizing the empirical rules for HEA design described above, a desktop study was undertaken in order to assess the viability of single-phase alloys for a wide range of elemental combinations – acknowledging that such rules are empirical and to be applied the description

of HEAs (and hence more specifically applied to compositionally complex alloys). The work herein was focused on the use of low-density elements (noting the density of elements in **Table S1**), with the criterion that they be lighter than pure iron (Fe). The desktop study was also limited to elements that were not flammable and capable of being processed by conventional methods (be it laser melting, spark plasma sintering, or arc melting). Interestingly, when using the empirical rules as a predictive tool, apparent single-phase alloy could be achieved by four elements, which is less than the common notion of requiring at least five elements. To this end, an important class of compositionally complex alloys was identified, namely the AlTiVCr system, which revealed a strong possibility to form simple solid solutions, as per the calculated parameters presented in **Table 1**. The more thorough exploration of this system however, using detailed characterization and first-principles modeling, to move beyond empirical rules and to a more general approach that can be applied universally, is presented.

2. Experimental

2.1 Material preparation

An equiatomic AlTiVCr alloy was produced by conventional arc melting under an argon atmosphere on a water-cooled copper hearth. The starting materials were pure (99.99 %) metal chunks, and the ingot was remelted several times for chemical homogeneity.

2.2 Characterization methods

X-ray powder diffraction (XRD) was used to determine the phase constitution of as-cast AlTiVCr. The alloy was ground first by hand using an agate mortar and pestle, and then in a McCrone Micronsing mill for ~30 seconds such that all of the powder passed through a 100

1 μm sieve. XRD data were collected on a PANalytical X'Pert PRO MPD in Bragg-Brentano
2 geometry [27], using a Co target tube operated at 40 kV and 40 mA. A graphite post-
3 diffraction monochromator was used to eliminate unwanted wavelengths and x-ray
4 fluorescence. The XRD data were analyzed using the Rietveld method [28], as implemented
5 in the software package TOPAS (Version 5, Bruker AXS).
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12 Microstructure characterization was carried out by scanning electron microscopy (SEM)
13 using an FEI Nova NanoSEM 450, transmission electron microscopy (TEM) using an FEI
14 Tecnai G2 T20 and FEI Tecnai G2 F20, as well as atom probe tomography (APT). SEM
15 samples were polished to a 1 μm diamond paste finish and then imaged in the backscattered
16 electron (BSE) mode. TEM specimens were prepared by focused ion beam (FIB) milling,
17 using an FEI Quanta 3D dual-beam FIB/SEM instrument. A thin foil was milled from a bulk
18 HEA specimen via Ga ion milling, followed by 'lift out' onto a Cu grid, and followed
19 subsequently by a thinning process of the foil to ~ 100 nm in thickness. Atom probe
20 specimens were also prepared using a FEI Quanta 3D instrument (Ga⁺ ion source) by in-situ
21 lift-out method [29].
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38 Atom probe experiments were conducted using a Local Electrode Atom Probe (LEAP) 4000
39 HR instrument (CAMECA Instruments Inc.) operating in voltage mode under ultra-high
40 vacuum at a temperature of 65 K, using a pulse fraction of 20 %, pulse repetition rate of 200
41 kHz, detection rate of 0.01 atoms per pulse and standing voltage during probing in the range
42 of 4.8 to 9.3 kV. Tomographic reconstruction and visualization of the APT data was
43 performed with the IVAS 3.6.8 software. The tip profile reconstruction method was
44 employed using SEM images taken after site-specific preparation, and the atomic density to
45 which the reconstructed volume was built was taken as that of Cr, since it represents an
46 approximate average when also taking into account the field evaporation potentials of the
47 four constituent elements.
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Vickers hardness was measured on polished surfaces using a Vickers hardness tester (Wolpert Wilson 432S), applying a load of 3 kg with a dwell time of 15 seconds and 6 replicate tests were conducted. The density of the alloy was measured using the standard Archimedes method using a balance with precision of 0.001 g.

2.3 First-principles calculations

First-principles calculations based on density functional theory (DFT) were employed by using the Vienna Ab-initio Simulation Package (VASP) [30] to determine the thermodynamic and structural properties of the AlTiVCr alloy. The projector augmented wave method (PAW) [31] and the exchange-correlation functional depicted by the generalized gradient approximation by Perdew, Burke, and Ernzerhof (GGA-PBE) [32] were employed. To increase the accuracy of the calculations, the plane wave energy cutoff was increased by a factor of 1.3 times the maximum energy of the pure elements. The energy convergence criterion of the electronic self-consistency was set as 10^{-7} eV/atom for all the calculations. For the calculations of the disordered BCC and B2 structures, a k -points grid of $10 \times 10 \times 10$ was applied. For the calculations of pure Al, V and Cr, the k -points grid was set as $20 \times 20 \times 20$. The structures were relaxed by implementing the Methfessel-Paxton method [32] in order to calculate the forces acting on the atoms, except for pure Ti, which was relaxed by implementing Gamma centered scheme with k -meshes of $20 \times 20 \times 15$.

In combination with the quasi harmonic approach, for a metallic phase with a fixed atomic distribution on the sublattice sites, its finite temperature thermodynamic properties can be depicted in terms of first-principles calculations [34,35]; wherein the Helmholtz free energy $F(V,T)$ at volume V and temperature T is given by:

$$F(V,T) = E_0(V) + F_{vib}(V,T) + F_{ele}(V,T) \quad (6)$$

$E_0(V)$, is a static energy at 0 K obtained by a fitting of the first-principles energy vs. volume data points based on a four-parameter Birch-Murnaghan equation of state (EOS) [34]. The second part, $F_{vib}(V,T)$, is the contribution of lattice vibration to the Helmholtz free energy, which is calculated based on the Debye-Grüneisen model [34] in the present work. The parameters needed in the Debye-Grüneisen model are obtained from the EOS fitting. The third part, $F_{ele}(V,T)$, represents the thermal electronic contribution, which is based on the first-principles electronic density of state (DOS) using Fermi-Dirac statistics [35].

For phases with atomic mixing on sublattices, such as BCC and B2 phases, the contribution of the compositional configurational entropy to the Helmholtz free energy should be included.

Thus, the total Helmholtz free energies of these two phases are given by:

$$F(V,T) = E_0(V) + F_{vib}(V,T) + F_{ele}(V,T) + \Delta TS_{mix} \quad (7)$$

where S_{mix} is the compositional configurational entropy, approximated as the ideal entropy of mixing. For the disordered BCC phase, the ideal entropy of mixing per mole of atoms is given by:

$$S_{mix}^{BCC} = -R \sum_{i=Al,Ti,V,Cr} x_i \ln(x_i) \quad (8)$$

where S_{mix}^{BCC} denotes the ideal entropy of mixing, R the gas constant, and x_i the mole fraction of each component element. For the B2 phase, based on the proposed sublattice model, Ti and V are mixed on one sublattice, while Al and Cr are mixed on another sublattice. Thus, the ideal entropy of mixing per mole of atoms is given as:

$$S_{mix}^{B2} = -\frac{1}{2} R(y_{Ti} \ln(y_{Ti}) + y_V \ln(y_V)) - \frac{1}{2} R(y_{Al} \ln(y_{Al}) + y_{Cr} \ln(y_{Cr})) \quad (9)$$

where S_{mix}^{B2} denotes the ideal entropy of mixing of the B2 phase, and y_{Ti} , y_V , y_{Al} and y_{Cr} denote the sublattice site fractions of Ti, V, Al and Cr, respectively, which all equal to 0.5. The $\frac{1}{2}$ factor accounts for the ratio of the sublattice site. In the results section below, the

application of the above first principles concepts are described as they pertain to simulation of
the AlTiCrV system.

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3. Results and discussion

3.1 Microstructural characterization

The density of the AlTiVCr alloy produced herein was measured to be 5.06 g cm^{-3} . This is in excellent agreement with the theoretical density of 5.08 g cm^{-3} , and significantly lighter than the ~ 6 to 8 g cm^{-3} of typical Fe containing HEAs and CCAs. For comparison, the theoretical density of a number of alloys was calculated by dividing the mass of the unit cell (determined by its occupant atoms) by the volume of the unit cell, and provided in Table S2.

XRD data collected from a powdered sample of the AlTiVCr alloy are shown in Figure 1. The peaks observed in the data indicate that the sample is composed of a single ordered B2 phase (space group $Pm-3m$) with a lattice parameter of $3.075 \text{ \AA}$ and a corresponding crystallographic density of 5.076 g cm^{-3} . However, it should be noted that it is not possible from XRD alone to rule out a mixed BCC-B2 microstructure based on such data, if the BCC phase were to have a very similar lattice parameter to the B2 phase. In order to gain some insight into the ordering responsible for the B2 superlattice peaks, the XRD data were analyzed by the Rietveld method [28]. As X-ray scattering factors scale linearly with atomic number, there is little contrast between the transition metals Ti, V and Cr. Therefore, in order to generate the intense superlattice peaks observed in the XRD data, a significant proportion of the much lighter Al atoms must segregate to a different superlattice site, compared with the transition metals. Assuming that the sample is indeed comprised of a single B2 phase, the degree of Al segregation can therefore be approximated by refining the site occupation factors in a model for the B2 phase. In such a model, a single mixing parameter is used to vary the concentration of Al atoms in the (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ sites from 25 % in both (disordered BCC structure) to 0 % in the (0,0,0) site and 50 % in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site (fully segregated), with the balance being the average of the transition metals. The results of this

analysis suggest that approximately 82 % of the Al atoms in the alloy segregate to the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site.

Scanning electron microscopy (SEM) (**Figure 2a**) reveals that the AlTiVCr alloy has a polycrystalline microstructure. The energy dispersive spectroscopy (EDS) mapping results (**Figure 2c-f**) of the magnified grain boundary area (**Figure 2b**) indicated that alloying elements are uniformly distributed for the length scale probed. Additionally, bright field TEM (**Figure 3a**) of the grain boundary area shows that there are no discernable secondary phases at the grain boundary region. The image contrast in **Figure 3a** corresponds to the apparently darker grain having been imaged along the [001] zone axis, while the comparatively brighter grain is imaged in an off-zone axis. Lattice-resolved TEM along the [111] zone axis in **Figure 3b** depicts that the lattice is uniform, and the minor contrast variations are attributed to slight deviations in thickness and strain. Selected area diffraction patterns (SADP) along the [001] (**Figure 3c**) and [011] zone axis (**Figure 3d**) reveal the existence of superlattice reflections, concomitant with the B2 phase, whereby the B2 phase is determined to have a lattice parameter of 3.08 Å (in excellent agreement with the corresponding XRD data). Dark field imaging (**Figure 4a**) using the (100) superlattice reflection of the SADP along [001] zone axis shows a domain-like structure, and the corresponding bright field image is provided in **Figure 4b**. However, from the high-angle annular dark field (HAADF) lattice image along the [001] zone axis (**Figure 4c**), there does not appear to be any obvious compositional contrast. In addition, Scanning TEM mapping using energy dispersive X-ray spectroscopy (**Figure 5a-d**) indicates the elements Al, Ti, V and Cr are uniformly distributed within the matrix.

3.2 Atom probe tomography

3.2.1 Atom probe maps and bulk composition

Atom probe tomography (APT) was conducted on this alloy in an attempt to quantify alloy ordering and provide information on compositional uniformity. The tomographic maps (**Figure 6**) show a highly uniform elemental distribution of Al, Ti, V and Cr. This uniformity was maintained upon solidification from the melt since the alloy was studied in the ‘as-cast’ condition. The atom probe mass spectrum is provided in **Figure 7**. AlH_2^+ and AlH_3^+ occur due to residual hydrogen in the vacuum chamber. These peaks have been labelled as Al for compositional determination; and composition percentages have been indicated where peak overlap occurs. Elements with the highest percentage are used for composition related to further spatial analysis where a single ion assignment is required for each peak. The bulk composition (at. %) derived from the APT data (**Table 2**) is consistent with the equi-atomic nature of the AlTiVCr alloy.

3.2.2 Nearest-neighbor analysis

The experimental distribution of 1st, 10th and 100th nearest neighbor (NN) distances between Al atoms is the same as that of the randomly labelled data (**Figure 8a**), which indicates that Al atoms are not clustered, but rather randomly distributed in solid solution. Ti, V and Cr atoms are similarly non-clustered and apparently randomly distributed in solid solution (**Figure 8b-d**). However, it is noted that such data cannot be further interpreted from the point of view of ordering (short- or long-range), which does not imply or require the atoms to be more or less closely spaced. Therefore, quantitative chemical-structure analysis of the experimental APT data has been carried out on the Characterization Virtual Laboratory [41] using recently developed generalized multicomponent short range order (GM-SRO) parameters [42-44].

3.2.3 GM-SRO analysis

Calculated values of the GM-SRO parameters are given in **Figure 9**, where a positive value is indicative of co-segregation in that crystallographic shell, and a negative value indicates anti-segregation of the two sets of elements. The smallest distance between atoms in a BCC unit cell is center to corner. This case represents the highest chance for NN segregation from the GM-SRO parameter perspective and relates to the positive values seen for V-Al, Cr-Al and Ti-Al (**Figure 9**). This means Al tends to be in the center of the body-centered structure, which is also supported by the Al-Al parameter being close to random (GM-SRO parameter = 0). Now, considering the corner to corner distance at the same edge of unit cell, this NN distance could appear as random because it is neither the smallest nor largest. From the GM-SRO results, we see that Al-(Al, Ti, V), V-V, Cr-Cr and Ti-Ti are all close to random for all shells. The largest distance is corner to corner in the opposite cube corners. This distance actually represents the next-NN distance since there is a body-centered atom in between, and atoms on the opposite cube corners to each other would therefore be represented by anti-segregation/ordering from the GM-SRO perspective. The GM-SRO results for the AlTiVCr CCA show that V-Ti, Cr-Ti, Ti-Cr display this trend/preference for these atoms not to be close to each other, and also Al-Cr and Ti-V to some degree (> 2nd shell).

3.3 First-principles calculations

In order to further understand the system studied beyond the simple set of empirical rules previously reported to relate to systems defined as HEAs, first-principles calculations were performed herein to investigate the structural and thermodynamic properties of AlTiVCr. This was considered essential given the apparent benefits of a four-component, light, single-phase alloy, in addition to presenting a framework that is suited to modeling of CCAs more generally. In framing the calculations, two types of 32-atom supercells, disordered BCC and the ordered B2 phase with disorder-mixing at individual sublattice sites, were built based on the special quasi-random structures (SQS) method [45-47]. The simulation supercell was

generated by using the Alloy Theoretic Automated Toolkit (ATAT) [47-48]. The SQS method provides good periodic supercell approximation to the true random solution phase under the constraint of a computationally tractable cell size N (where N is the number of atoms per supercell). To date, SQSs with $N \leq 36$ were successfully generated for random binary and ternary alloys [49-52], and have been shown to give reliable electronic and thermodynamic properties of the random solution phases [53-56]

As the only B2 phase previously reported in the sub-systems of the AlTiVCr quaternary is $\text{Ti}_{0.5}(\text{Cr},\text{Al})_{0.5}$ [57], the sublattices model of the B2 phase studied in the present work was simplified as $(\text{Ti},\text{V})_{0.5}(\text{Cr},\text{Al})_{0.5}$ to balance the equal molar composition. As described in the method section, the Helmholtz free energy $F(V,T)$ of the disordered BCC phase, the B2 phase and the four pure elements were obtained as a function of volume and temperature in terms of first-principles calculations. At zero pressure, the thermodynamic quantities of interests are derived as a function of temperature from the obtained Helmholtz free energy based on the thermodynamic relationships given by:

$$B(T) = V_0(T) \left(\frac{\partial^2 F}{\partial V^2} \right)_T \quad (10)$$

$$H(T) = F(T) - T \left(\frac{\partial F}{\partial T} \right)_{V=V_0} \quad (11)$$

$$S(T) = - \left(\frac{\partial F}{\partial T} \right)_{V=V_0} \quad (12)$$

where $V_0(T)$ is the equilibrium volume under zero pressure, $B(T)$ the bulk modulus, $H(T)$ the enthalpy and $S(T)$ the entropy. In addition, the lattice parameter $a_0(T)$ is calculated from $V_0(T)$. The calculated equilibrium volume, lattice parameter and bulk modulus of the disordered BCC and B2 phase at 300 K are listed in the **Table 3**. The calculated lattice parameter (3.06 Å) of the B2 phase at 300 K is consistent with the experimentally determined lattice

parameter (3.08 Å) calculated from SADP herein. The bulk modulus of the B2 phase was calculated to be 151.6 GPa at 300 K.

The formation enthalpy of both the disordered BCC and B2 phases is given by:

$$\Delta H_f(X) = H(X) - \frac{1}{4}H(Al) - \frac{1}{4}H(Ti) - \frac{1}{4}H(V) - \frac{1}{4}H(Cr) \quad (13)$$

where X denotes either the disordered BCC phase or the B2 phase, ΔH_f is the formation enthalpy, and H 's are the finite temperature enthalpies per mole of atoms of the disordered BCC phase, the B2 phase, and the four pure elements obtained based on equation 8. The reference states are set as FCC for Al, HCP for Ti, BCC for V and Cr, namely, the stable structures of these pure elements at the temperature of 298.15 K and the pressure of 1 bar. By analogy, the formation entropy ΔS_f is given as:

$$\Delta S_f(X) = S(X) - \frac{1}{4}S(Al) - \frac{1}{4}S(Ti) - \frac{1}{4}S(V) - \frac{1}{4}S(Cr) \quad (14)$$

where S 's are the entropies per mole of atoms obtained based on Equation 12. The calculated ΔH_f and ΔS_f of these two phases are shown in **Figure 10a** as a function of temperature. With a wide range of temperature, there is only a small decrease in ΔS_f , whilst ΔH_f becomes slightly more negative for both phases. In addition, in order to identify the relative stability between the disordered BCC and B2 phases, the Gibbs energy of formation at finite temperatures is determined by the following equation:

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (15)$$

As shown in **Figure 10b**, the B2 phase has a more negative Gibbs energy of formation up to 900 K, which indicates it is more stable than the disordered BCC phase at low temperature. However, these two curves have a tendency to cross at high temperature, implying that the disordered BCC phase will be more stable at higher temperature due to the contribution of entropy. Thermogravimetric analysis (TGA) validates the thermal stability of the AlTiVCr alloy in the range from 300 K to 900 K since there is no obvious phase change (**Figure S3**).

For the sake of reading convenience, ΔH_f , ΔS_f , and ΔG_f of the disordered BCC and B2 phase at 300 K are also listed in **Table 3**. The DFT analysis has validated the existence of a four-element, light-weight AlTiVCr HEA, with a B2 structure. The alloy therefore, as predicted from empirical relationships, is indeed a uniform single-phase compositionally complex alloy comprised of the B2 phase. The alloy also exhibits an exceptionally high hardness of ~500 HV, ascribed to the B2 structure [4, 39].

4. Conclusions

A lightweight AlTiVCr compositionally complex alloy has been presented herein ($\rho = 5.06 \text{ g cm}^{-3}$) based on the use of only four principal elements. The AlTiVCr alloy exhibits a simple single-phase microstructure consisting of B2 phase, and was produced by elements common to ingot metallurgy and production was non-flammable and non-hazardous via arc melting. The analysis herein indicates that a greater negative Gibbs energy of formation of the B2 phase indicates that this phase is more stable than the disordered BCC phase over a wide range of temperatures, and this was confirmed by XRD, HRTEM and APT. It was also shown that DFT calculations, the methodology of which was presented here, have significant merit in the prediction and understanding of phases in compositionally complex alloys.

From the characterization perspective, it was revealed that detailed Rietveld analysis was beneficial in the study of compositionally complex alloys, and such application to the present AlTiVCr system was demonstrated. Furthermore, the coupling of APT and DFT analysis was able to aid in the identification of lattice site occupancy, which provides a detailed and unambiguous characterization of alloy structure, and is an important methodology as applicable to the detailed study of compositionally complex alloys and so-called high entropy alloys alike.

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Table 1. Experimental density and phase prediction parameters for AlTiVCr alloy. δ is the atomic size parameter, Ω indicates the solid solution formability.

Alloy	ρ (g cm ⁻³)	δ	ΔH_{mix} (kJ mol ⁻¹)	ΔS_{mix} (J K ⁻¹ mol ⁻¹)	Ω
AlTiVCr	5.06	6.4%	-16.75	11.5	1.25

Table 2. Bulk composition (at. %) of APT data corresponding to **Figure 7**.

	Al	Ti	V	Cr
Composition related to spatial analysis	25.40	25.44	23.08	25.84
Decomposition of peak overlap	25.21 ± 0.02	26.60 ± 0.02	22.82 ± 0.02	23.62 ± 0.02

Table 3. Calculated thermodynamic and structural parameters of AlTiVCr alloy with BCC and B2 structure at 300 K.

Structure	V_0 ($\text{\AA}^3/\text{atom}$)	a_0 ($\text{\AA}$)	Bulk modulus (GPa)	ΔH_f (kJ mol^{-1})	ΔS_f ($\text{J K}^{-1} \text{ mol}^{-1}$)	ΔG_f (kJ mol^{-1})
Disordered BCC	14.35	3.06	146.6	-1.19	10.09	-4.22
B2: (Ti,V) _{0.5} (Cr,Al) _{0.5}	14.31	3.06	151.6	-9.28	3.55	-10.34

Figure 1. X-ray diffraction pattern from a powdered sample of the as-cast AlTiVCr alloy. Observed (I_{obs}), calculated (I_{cal}) and differential (I_{dif}) intensities are shown in green, red and grey respectively. The difference pattern was obtained by $I_{obs} - I_{cal}$. Peaks corresponds to the B2 phase are labelled.

Figure 2: a) Backscattered secondary electron image of as-cast AlTiVCr alloy, b) magnified grain boundary area indicated by the arrow in a), c-f) EDS mapping results of the grain boundary area reveal that Al, V, Ti and Cr are uniformly distributed.

Figure 3. a) Bright field image of grain boundary area of as-cast AlTiVCr alloy, the darker grain is along the [001] zone axis while the brighter grain is off zone, b) Lattice image of as-cast AlTiVCr alloy along [111] zone axis using conventional TEM, Selected area diffraction patterns (SADPs) along the c) [001] and d) [011] zone axis reveal a B2 phase with a lattice parameter of 3.08 Å.

Figure 4. a) Dark field TEM image using the (100) superlattice reflection of the SADP along [001] zone axis, and b) corresponding bright field TEM image. c) High-angle annular dark field (HAADF) lattice image along [001] zone axis using STEM mode.

Figure 5. STEM mapping of as-cast AlTiVCr alloy revealing that a) Al, b) Ti, c) V and d) Cr, are uniformly distributed.

Figure 6. Tomographic maps showing the elemental distribution of Al, Ti, V and Cr. Smaller volumes ($35 \times 35 \times 70 \text{ nm}^3$) were taken from the whole data sets in order to avoid Ga ion implantation (near the top of the specimen tip) from focused ion beam sample preparation.

Figure 7. Atom probe mass spectrum (voltage mode) for the AlTiVCr alloy.

Figure 8. Histograms of 1st, 10th and 100th nearest neighbor (NN) distances between a) Al atoms, b) Ti atoms, c) V atoms and d) Cr atoms.

Figure 9. Chemically specific GM-SRO parameters for the first 12 nearest-neighbor shells, calculated from the experimental APT data.

Figure 10. a) Formation entropy ΔS_f and formation enthalpy ΔH_f of AlTiVCr with BCC and B2 structure as a function of temperature. b) Gibbs energy of formation ΔG_f of both BCC and B2 phase as a function of temperature.

Graphical abstract