Structural stability of Cubic Ti_2AlV and Tetragonal $TiAl_2V$ using First Principle Calculations

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Abstract. TiAlV intermetallic alloys are used as key functional materials in various industries due to their superior properties. However, our understanding of their structural phase stabilities is still limited and remains confined. In this work density functional theory approach was employed to investigate the structural and electronic stability of cubic Ti_2AlV and tetragonal $TiAl_2V$ phases. The stabilities of these structures were determined by calculating the heats of formation and electronic properties. The calculated heats of formation values revealed that both phases are thermodynamically stable since $\Delta H_f < 0$. Moreover, it was found that the $TiAl_2V$ structure is energetically more stable than Ti_2AlV. Also, the partial density of states was studied to investigate the electronic properties.

1. Introduction

Ti-Al-V-based alloys are widely employed in biomedical, aerospace, automotive, space, and other important industries. This is due to their low density, high strength, and good corrosion resistance requirements [1, 2]. Many investigations have shown that heat treatment would promote microstructures of Ti-Al-V alloys, allowing for superior mechanical properties. A better understanding of the structure and morphology of precipitates can further improve the strength of alloys [3]. These alloys are available in binary AB and ternary A2BC stoichiometric compositions. Deviations from the stoichiometric composition are accommodated by vacancies on the various sublattice sites and/or antisites [4].

The effect of structural qualities, however, varies. As a result, it is vital to investigate the intrinsic properties of each phase as well as their impact. Banerjee *et al.* [5] investigated the chemical compositions and microstructures measured across the Ti_8Al_xV grade. They reported that the volume fraction of the alpha phase decreased with an increase in the V content, and the volume fraction of the beta phase increased. Furthermore, the microstructure and mechanical properties of Ti-Al-V powder have been investigated. It has been reported that the microstructure of equiaxed to columnar grains varies. Moreover, as the mass content of Al increases, the beta grain size decreases [6].

First principle calculation was used to study the site occupancy of the B2 phase in Ti_2AlX (X= V, Cr, Fe, Mo, Ta, Nb, Zr, Hf and Re) intermetallic [7]. According to their findings, all the alloys were found to be thermodynamically stable, and the formation energy results indicated that the B2 phase is the most stable. Wan *et al.* [8] studied the structural and electronic properties of second phases and solid solutions in Ti-xAl-yV alloys using First principle approach. The formation enthalpy for the alpha and beta phases was found to be -0.295 and 62.786 eV. atom^{-1}, respectively. Therefore, it was stated that the alpha phase has greater structural and formation stability than the beta phase due to its lower formation enthalpy. This indicated that the Ti-Al-V α phase has the strongest alloying ability and structural stability. The structural phase is one of the most important measures for controlling the properties of a material and causing a significant change in performance. As a result, it is necessary to investigate the properties of various phases.

In the present study, the structural and electronic properties of the cubic (Ti_2AlV) and tetragonal ($TiAl_2V$) crystals were investigated using density functional theory calculations. To characterize the structures, the heats of formation and electronic properties of the two phases were calculated. The current findings will provide theoretical insight into the thermodynamic comparison of the Ti_2AlV and $TiAl_2V$ compositions.

2. Computational Setup

Cambridge Series Total Energy Package (CASTEP) code [9], as implemented in Material Studio software, was used for all density functional theory calculations [10, 11]. To calculate the geometry optimization, a generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correction functional was used [12]. Geometry optimization calculations were employed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The Monkhorst-Pack scheme [13] was used to integrate the k-points. Cut-off energy was set to 600 eV with k-points of 6 × 6 × 6 and 6 × 6 × 5 for both cubic and tetragonal structures. The maximum force tolerance and displacement were set at 0.03 eV and 10^{-3}, eV. atom^{-1}, respectively. Heats of formation (ΔH_f) of $TiAl_2V$ and Ti_2AlV structures were calculated as follows:

$$\Delta H_f = E_{tot} - \sum_i n_i E_i \tag{1}$$

whereby, E_{tot}. and E_i are the total energies of crystal structures (Ti_2AlV and $TiAl_2V$) and individual atoms (Ti, Al and V). The n_i represents the number of an atomic configuration of the element.

3. Results and Discussion

3.1. *Crystal structures and Heats of formation*

The intermetallic alloy of TiAlV mostly consists of two crystal structures which are face-centred tetragonal (L10) and face-centred cubic. It is noted that the face-centred tetragonal is an Al-rich crystal with chemical formula $TiAl_2V$ and cubic structure is defined as Ti-rich phase Ti_2AlV, crystalizes in P4/mmm and F-43M space group, respectively. Figure 1 illustrate the atomic crystal structures of these phases, $TiAl_2V$ and Ti_2AlV. The bulk properties of these two crystals were calculated and the results are presented in Table 1. The equilibrium lattice parameter of Ti_2AlV is a = 6.337 Å and $TiAl_2V$ a= 5.469 Å and c/a= 1.45 Å. The obtained parameter for Ti_2AlV is in good agreement with the value previous results [14]. If the c/a ratio is 1/2, the pseudo-cubic tetragonal phase is formed, as referred to in the literature [15]. The equivalent c/a ratio value of 1.45 was obtained in the current study.

Structural stability of $TiAl_2V$ and Ti_2AlV were analyzed using heats of formation (ΔH_f), which is defined as the energy required to form the phase crystal from single atoms. A lower formation energy of the crystal structure implies more structural stability. Heats of formation per atom for the two phases were calculated using Eqn. 1 and the results are shown in Table 1. The calculated ΔH_f of Ti_2AlV and $TiAl_2V$ structure is -0.121 eV. atom^{-1} and -0.412 eV. atom^{-1}, respectively. A negative ΔH_f value for both structures indicates the possibility of these two phases forming spontaneously, implying thermodynamic stability. Our current findings on heats of formation value for Ti_2AlV structure agree well with the previously reported values (-0.112 eV. atom^{-1}) [7]. However, the $TiAl_2V$ structure was found to have the lowest ΔH_f, indicating that the tetragonal phase shows higher structural stability than cubic. As a result, it is possible to deduce that $TiAl_2V$ crystal has stronger stability and forming capacity than Ti_2AlV. This is in line with the fact that the alpha phase of Ti-Al-V solid solution has a greater capacity to form than the beta phase [8].

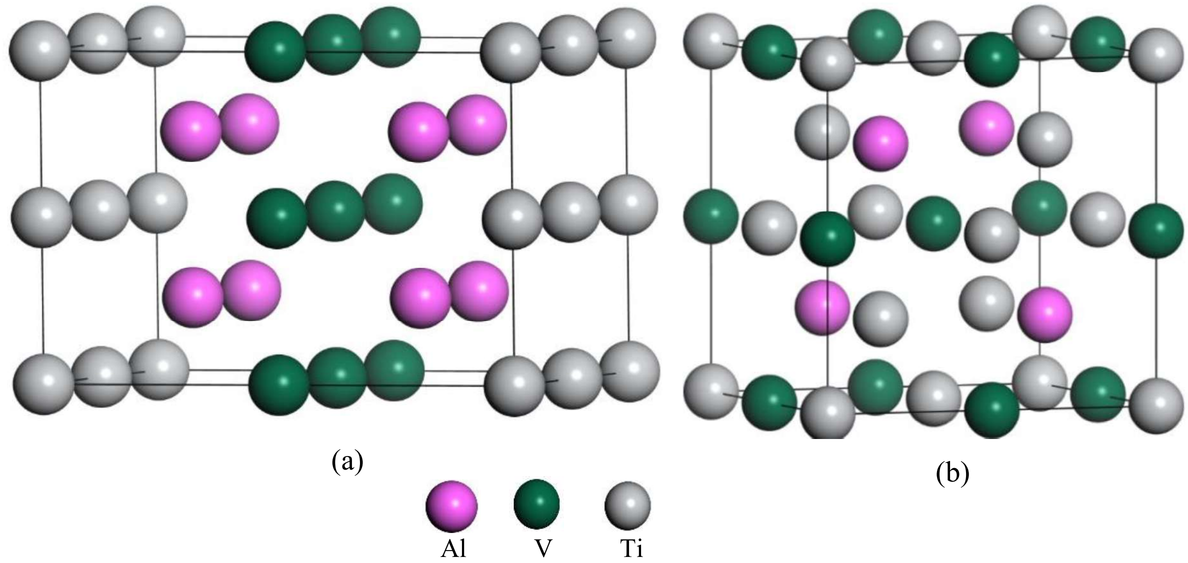

Figure 1. Optimized crystal structure of (a) tetragonal (t-$TiAl_2V$) and (b) cubic (c-Ti_2AlV) phase.

Table 1. The calculated heats of formation (ΔH_f), present and previous lattice parameters for cubic and tetragonal structures.

structures	methods	*a (Å)*	*c/a*	V(Å^3)	ΔH_f (eV. atom^{-1})
c-Ti_2AlV	present	6.337		254.4	-0.121
	previous	6.337 [14]	-		-0.112 [7]
t-$TiAl_2V$	present	5.469	1.45	244.2	-0.412

3.2. Density of states

To further understand the electronic properties and interaction for both cubic and tetragonal structures, partial and total density of states (PDOS) are investigated. PDOS and TDOS curves are presented in Figure 2 and Figure 3, respectively. This DOS plot highlights the contribution of different atoms and orbitals. We noted that all in all structures, the main peak at the fermi level is most contributed from the -d orbital from the 3d orbital of Ti and V atoms, while less contribution was noted from the -p orbital. This observation indicated that both structures have metallic behaviour. Moreover, the conductive region/side mostly consists of 3d (Ti and V) hybridize with the -2p Al atom. This shows the bonding character displayed by Ti-Al, Ti-V and Al-V from the hybridization between the lone pair in the -2p and -3d individual atoms. Both DOSs of these compounds display a deep pseudo-gap right above the Fermi level, this is due to a strong covalent interaction between the atoms. In addition, Figure 3 presents the TDOS curves for the two compounds, it was observed that the TDOS curve for $TiAl_2V$ lies lower at the Fermi level (E_F) whereas the E_F for Ti_2AlV is higher on the TDOS curve. This suggests that the FCT $TiAl_2V$ crystal is more stable than the FCC Ti_2AlV crystal which supports the stability trend observed in the heats of formation values. The cubic system's Fermi level is typically located in the middle of the DOS peak. The high TDOS near E_F, on the other hand, causes high energy, which leads to poor structural stability in the cubic state [16].

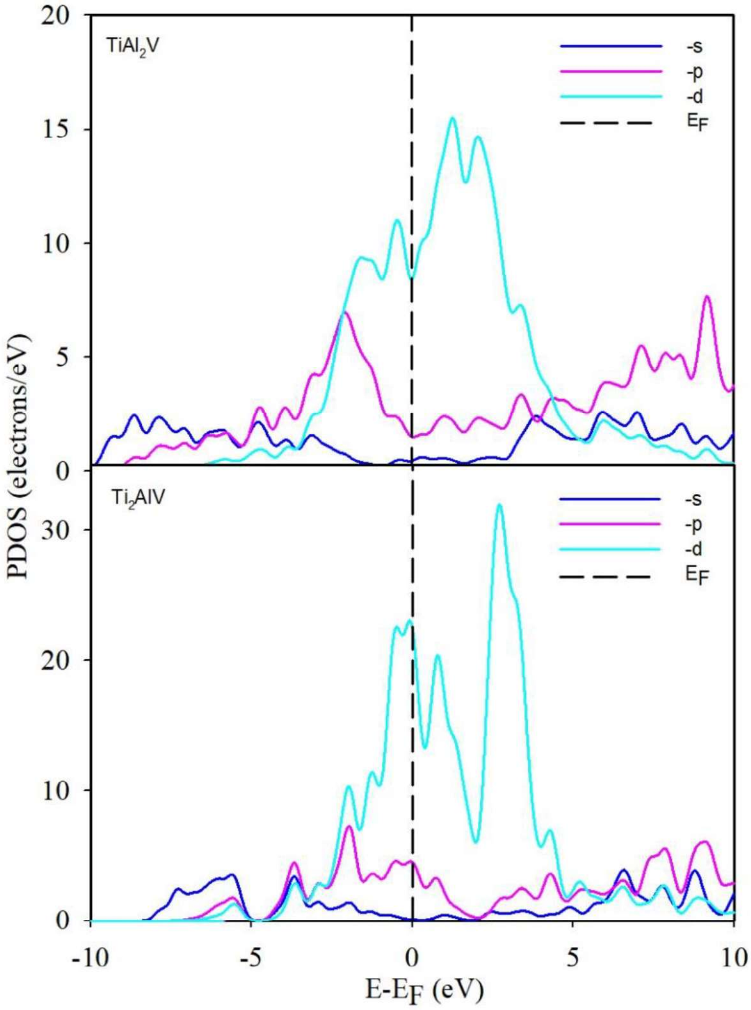

Figure 2. Partial density of states (PDOS) calculated for tetragonal (TiAl$_2$V) and cubic (Ti$_2$AlV) structures.

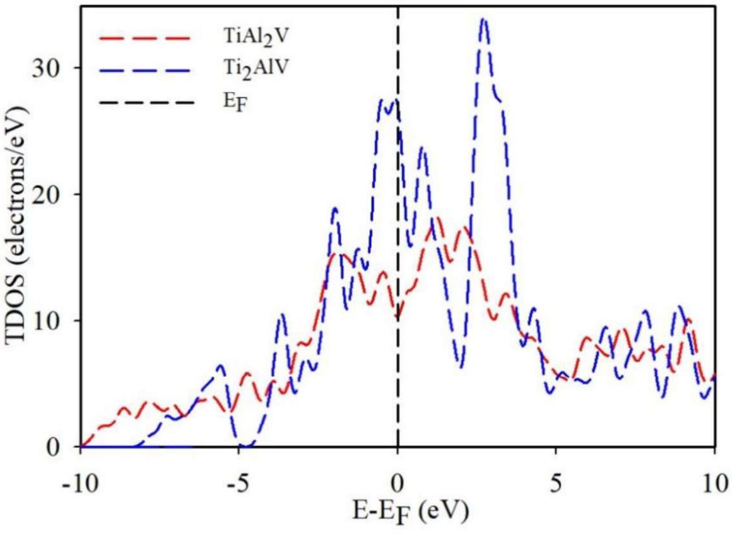

Figure 3. Total density of states (TDOS) plot for cubic (Ti$_2$AlV) and tetragonal (TiAl$_2$V) structures.

4. Conclusion

In summary, density functional theory calculations were successfully utilized to investigate the structural stability of Ti_2AlV and $TiAl_2V$ compounds. Both structures were discovered to be thermodynamically stable, having negative values for heats of formation. The calculated heats of formation values indicated that $TiAl_2V$ had a strongest structural stability than Ti_2AlV. According to electronic calculation, it was observed that the TDOS curve for $TiAl_2V$ lies lower at the Fermi level than the Ti_2AlV compound. This implies that the tetragonal phase ($TiAl_2V$) is structurally more stable than the cubic phase (Ti_2AlV).

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