

# First principle study of Ti<sub>50</sub>Al<sub>50</sub> alloys

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**Abstract.** The study on the Ti-based materials and its application has been the interest of many research industries. These alloys are known to have an ordered B2 phase at high temperatures and transform to a stable low B19 martensitic phase. First principle approach has been used to study L1<sub>0</sub>, B32, B2 and B19 Ti<sub>50</sub>Al<sub>50</sub> alloys and the results compared well with the available experimental data. The equilibrium lattice constants are in good agreement with the experimental values (within 3% agreement). Furthermore, the elastic constants of these alloys are calculated, and revealed stability for L1<sub>0</sub> and B19 structures, while B2 and B32 gave  $C' < 0$  (condition of instability).

## Introduction

The intermetallics involving aluminum and early transition metals are known to have many attractive properties, making them desirable candidates for high temperature structural applications. Some of the properties include low density, excellent high-temperature strength, high specific stiffness and good oxidation resistance [1, 2, 3]. Extensive studies of the microstructures, plasticity and effects of alloying elements on mechanical properties have been carried out world-wide. However, there are still obstacles to the successful use of two-phase TiAl alloys in structural applications, and one significant barrier is that their room-temperature tensile ductility is low [4]. It is well known that residual stresses play a role in determining the mechanical properties of materials. Therefore, it is necessary to study the distribution and variation of the residual stresses in TiAl-based alloys.

In the current study we have investigated the relative structural stabilities of the TiAl alloys. The heats of formation calculations revealed L1<sub>0</sub> structure to be more stable as compared to other structures due to its lowest formation energy and is consistent with the experimental results. The elastic constants and the phonon dispersions are also calculated

## Methodology

The calculations were carried out using *ab initio* density functional theory (DFT) formalism as implemented in the Vienna *ab initio* simulation code VASP [5, 6, 7, 8] with the projector augmented wave (PAW) [9]. An energy cutoff of 500 eV was used, as it was sufficient to converge the total energy of the TiAl alloys. For the exchange-correlation functional, the generalized gradient approximation of Perdew and Wang (GGA-PBE) [10] was chosen. The Brillouin zone integrations were performed for suitably large sets of *k*-points according to Monkhorst and Pack Pack [11]. The phonon dispersion spectra were evaluated using PHONON code [12] as implemented by Materials Design within their MedeA software, VASP code. All the calculations were done at 0 K.

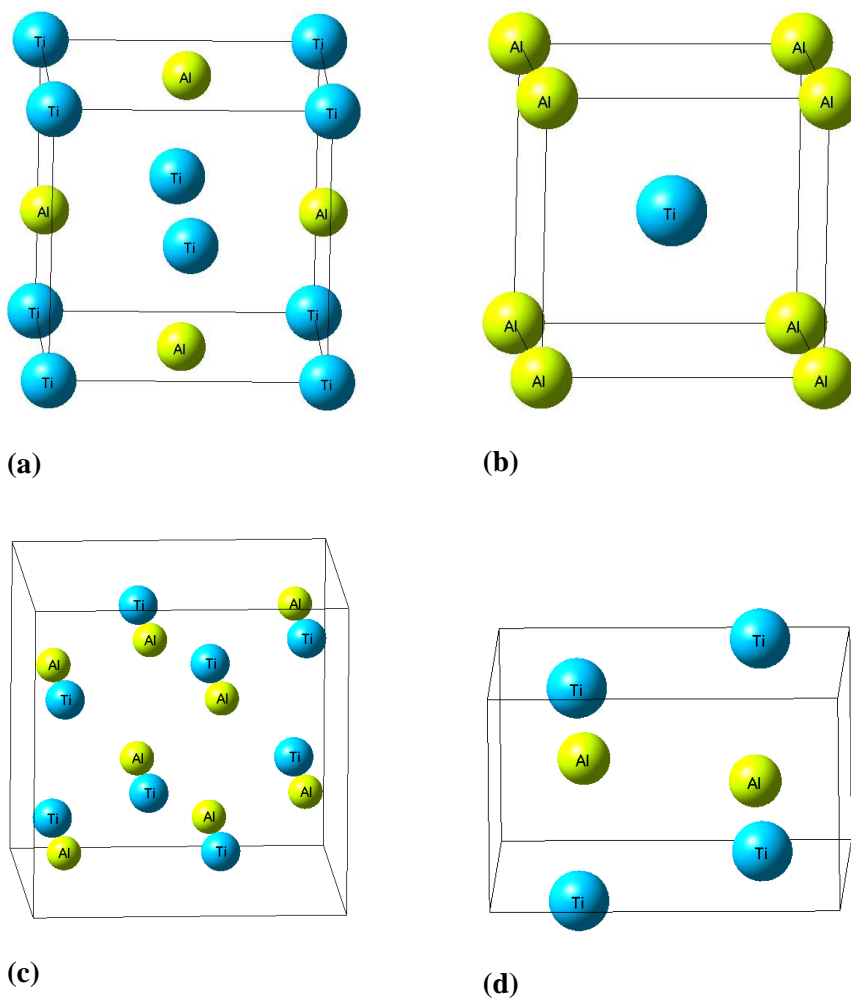
## Results and discussions

In Fig. 1, the investigated crystal structures of L1<sub>0</sub>, B32, B2 and B19 Ti<sub>50</sub>Al<sub>50</sub> are shown. In Table 1, we show the geometry information on symmetry and prototype; DFT results on equilibrium lattice constants and predicted heats of formation for the binary Ti<sub>50</sub>Al<sub>50</sub> alloys. The structures were subjected to full geometry optimization, allowing both the lattice parameters and volume to change.

Their relaxed lattice parameters are compared with the available experimental results. It was found that the lattice parameters are well reproduced to within 3% agreement with the available experimental and theoretical information. The heats of formation ( $\Delta H_f$ ), of the intermetallic phases are calculated according to the relation [13, 14, 15],

$$\Delta H_f = E^{TiAl} - [(1 - x)E_{solid}^{Ti} + xE_{solid}^{Al}], \quad (1)$$

where  $E^{TiAl}$ ,  $E_{solid}^{Ti}$  and  $E_{solid}^{Al}$  are the total energies of an intermetallic alloy, and elemental Ti and Al in their respective ground-state crystal structures, while  $x$  and  $1-x$  refers to the fractional concentrations of the constituent elements.



**Figure 1: The structures of (a) L10, (b) B2, (c) B32 and (d) B19 Ti<sub>50</sub>Al<sub>50</sub>**

**Table 1: The general geometry analysis information of the investigated Ti<sub>50</sub>Al<sub>50</sub> structures, their equilibrium lattice parameters (Å) and heats of formation ΔH<sub>f</sub> (eV/atom).**

Structure	Spacegroup	Pearson symbol	prototype	Lattice Parameters (Å)		ΔH <sub>f</sub> (eV/atom)	
				VASP	experimental	VASP	experimental
L1 <sub>0</sub>	P4/mmm	tP4	AuCu	a= 3.975 c= 4.083	3.975 [14] 4.068	-0.406	-0.391 [12]
B32	Fd-3m	cF16	NaTl	a= 6.369	-	-0.073	-
B2	Pm-3m	cP2	CsCl	a= 3.181	3.185 [15]	-0.264	-0.274 [9]
B19	Pmma	oP4	AuCd	a= 4.618 b= 2.857 c= 4.891	4.650 2.828 4.940	-0.363	

L1<sub>0</sub> Ti<sub>50</sub>Al<sub>50</sub> has the lowest heats of formation compared to other phases and is considered as the most stable structure in agreement with experimental observations. The structure has the lowest heats of formation of -0.406 eV and is comparable with the experimental value of -0.391 eV [14]. The orthorhombic B19 structure is found to be stable as compared to B32 and B2 phases which have the highest heats of formation of -0.073 and -0.264 eV, respectively. The results are comparable with the available experimental data as shown in Table 1. In Table 2, the calculated elastic properties of the Ti<sub>50</sub>Al<sub>50</sub> structures are shown. The accurate calculation of elasticity is important for determining the mechanical stability and elastic properties of any system. There are three ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ), six ( $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{66}$ ), nine ( $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$ ,  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ) and thirteen ( $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$ ,  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ,  $C_{15}$ ,  $C_{25}$ ,  $C_{35}$ ,  $C_{46}$ ) independent elastic constants for cubic, tetragonal and nine and thirteen, respectively. The mechanical stability criteria of cubic system as outlined elsewhere [16] is given as follows:

$$C_{44} > 0, C_{11} > |C_{12}| \quad \text{and} \quad C_{11} + 2C_{12} > 0, \quad (2)$$

The corresponding mechanical stability criteria for tetragonal crystal read as

$$C_{44} > 0, C_{66} > 0, C_{11} > |C_{12}| \quad \text{and} \quad C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} > 0, \quad (3)$$

While that for the orthorhombic crystal, the mechanical stability conditions are given by [16],

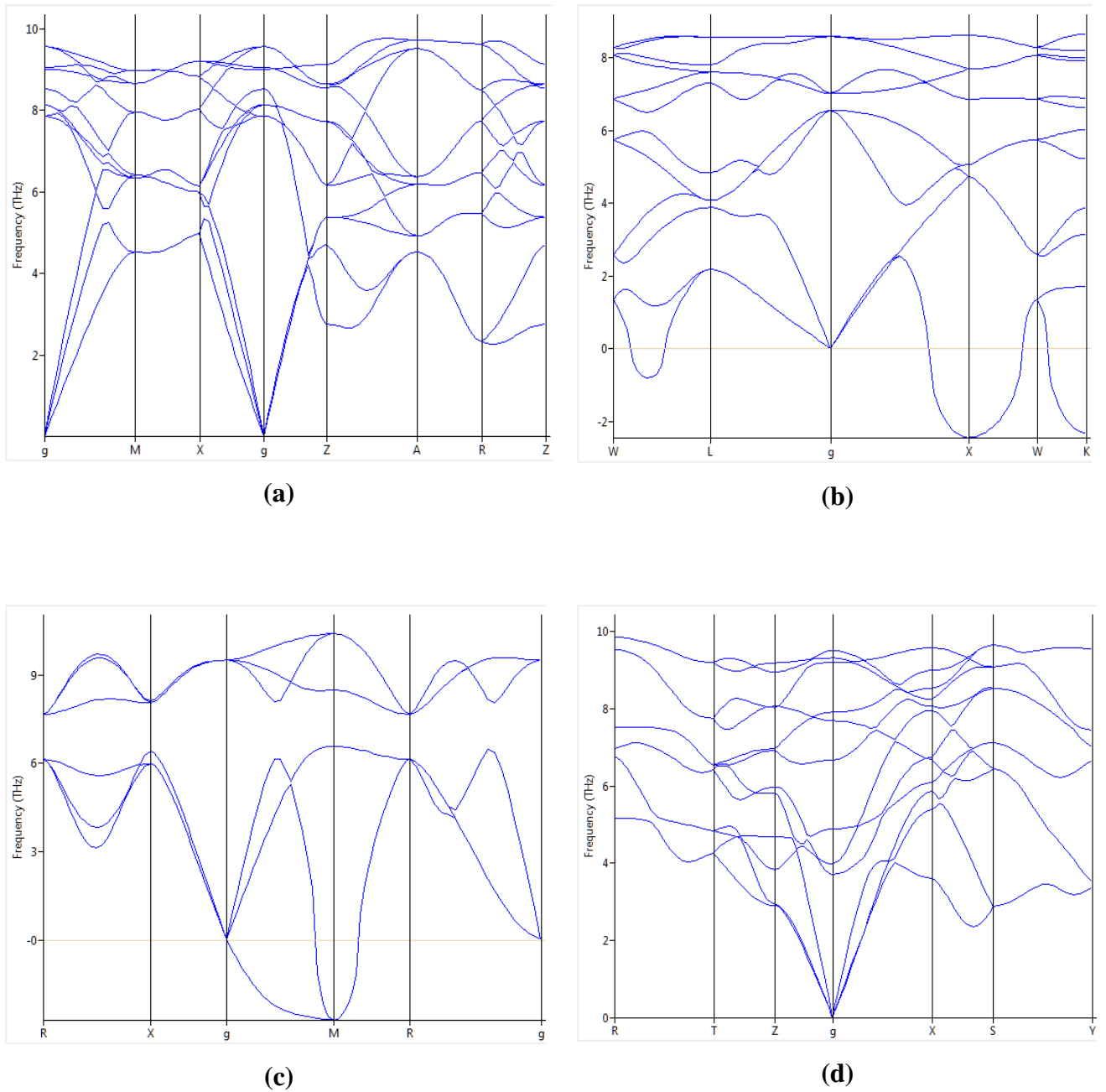
$$C_{11} + C_{12} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0, C_{22} + C_{33} - 2C_{13} > 0, C_{11} > 0, \\ C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0. \quad (4)$$

In order for the structure to be considered stable, the stability criterion for the elastic constants should be satisfied. In principle, the positive  $C'$  indicates the mechanical stability of the crystal, otherwise unstable. We observe from Table 2 that the L1<sub>0</sub> and B19 structures are mechanically stable with respect to the elastic constants since all the moduli are positive. Furthermore, we notice that the  $C_{11}$  is less than  $C_{12}$  for both B32 and B2 which result in a negative shear modulus ( $C' < 0$ ). These structures are thus considered unstable with respect to the stability criterion. In order to investigate the ductility, hardness and plasticity of these phases we calculated their bulk ( $B$ ), shear ( $G$ ), Young's ( $E$ ) moduli. The bulk moduli of both L1<sub>0</sub> and B19 structures is found to be larger than those of B32 and B2, suggesting that the later have higher strength. Pugh [17] proposed an empirical criterion which requires that  $G/B$  be less than 0.57 for ductility and  $G/B$  be greater ( $>0.57$ ) for brittleness. The  $G/B$  for both tetragonal L1<sub>0</sub> and orthorhombic B19 phases are slightly more than 0.57 which suggests that the structures are brittle, and hence have the highest Young's modulus  $E$ .

**Table 2: Elastic constants  $C_{ij}$ , bulk  $B$ , Young's  $E$  and shear modulus  $G$  (GPa) and the ratio of  $G/B$  of Ti<sub>50</sub>Al<sub>50</sub> structures**

$C_{ij}$	<b>L1<sub>0</sub></b>	<b>B32</b>	<b>B2</b>	<b>B19</b>
$C_{11}$	177	82	82	215
$C_{12}$	88	123	131	75
$C_{13}$	87			49
$C_{22}$				201
$C_{23}$				76
$C_{33}$	178			231
$C_{44}$	113	64	68	69
$C_{55}$				59
$C_{66}$	65			74
$C'$	44	-20	-24	70
$B$	117	110	115	116
$E$	188	83	86	176
$G$	75	30	31	70
$G/B$	0.64	0.28	0.27	0.60

We further determined the phonon dispersions of the structures and the plots are shown in Fig. 2. Interestingly, both the L1<sub>0</sub> and B19 structures do not show soft mode in the lower frequency (negative vibration) suggesting that these vibrational stability of the phases. This agrees well with the predicted elastic stability. Both B32 and B2 phases are unstable since they display soft modes along high symmetry directions (B32 in X and W-L; B2 along M direction) in the Brillouin zone.



**Figure 2: The phonon dispersion curves of (a) L1<sub>0</sub>, (b) B32, (c) B2 and (d) B19 Ti<sub>50</sub>Al<sub>50</sub>**

## Conclusion

First principle approach was used to study the stability of the L1<sub>0</sub>, B32, B2 and B19 at Ti<sub>50</sub>Al<sub>50</sub> atomic composition. The calculated lattice parameters are in good agreement with the available experimental results. We found good correlations between the elastic stability and phonon dispersion curve, consistent with the thermodynamic stability. L1<sub>0</sub> was found to be the most stable phase with the lowest heats of formation which are comparable with the experimental value; while the B32 was the least stable with the  $\Delta H_f$  of -0.073 eV. Interestingly both L1<sub>0</sub> and B19 were found to be mechanically stable with all elastic constants being positive. In addition their phonon dispersions curves showed no soft modes suggesting the stability of the phases. Both B32 and B2 have  $C_{11} < C_{12}$  leading to a negative  $C'$ . The ratio of G/B for L1<sub>0</sub> and B19 was found to be more than 0.57, suggesting the brittleness of the phases according to Pugh [17].

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