

First-principles study to explore the possibility of inducing martensitic transformation in ordered B2 TiRu phase by alloying with Pd

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Abstract

Density functional theory (DFT) based on the first-principles technique, CASTEP, was used to explore the possibility of inducing martensitic transformation (MT) in a stable B2 TiRu alloy by systematic introduction of palladium (Pd) on the ruthenium (Ru) site. The structural, mechanical and electronic properties of pure, as well as, Pd-doped TiRu were calculated. The elastic constants obtained show that the addition of Pd seems to induce MT in the ordered TiRu, as shown by mechanical instability ($C' = C_{11} - C_{12} < 0$) of the B2 phase against shear deformation at 0 K. This is an indication that B2 is likely to transform to low symmetry phases such as L1₀/B19'/B19'. Moreover, the calculated total density of states (T-DOS) also indicated that the addition of Pd shifted the Fermi level (E_F) from the centre of the pseudogap of the ordered pure TiRu towards the right (anti-bonding region), rendering the resulting B2 ternary phase unstable at certain Pd compositions higher than 10 atomic percent (at.%). The predicted induced martensitic transformation is one of the key characteristics of shape memory behaviour in B2 Ti-based alloys such as NiTi, TiPd and TiPt. Further work on the possible low temperature phases resulting from B2 Ti-Ru-Pd ternary alloys is underway.

Keywords: DFT-based first-principles technique, elastic properties, electronic structure, martensitic transformation (MT)

1. Introduction

Titanium (Ti) is an important engineering material for components of various applications ranging from biomedical, aerospace and automotive industries,^{1,2} where the high strength to weight ratio and high resistance to corrosion render Ti and its alloys attractive and ideal.¹ Ti-based intermetallic compounds are promising materials for high temperature applications as structural (heat and corrosion resistance) or non-structural materials (electronic devices, superconductors, etc.).^{1,3,4,5}

Addition of platinum-group metals (PGMs) to several alloys produced commercial alloys over the past 4-5 decades for the purpose of improving corrosion resistance and other functional properties.^{6,7} Being noble and high temperature stability enables PGMs as candidates of choice for high temperature structural application. Such materials find use in automotive exhaust system and in the manufacturing of high quality glass and glass fibres industries as they present high corrosion and oxidation resistance [8]. Among the PGMs, ruthenium (Ru) is the cheapest and the most reactive, hence it receives most of its application in chemical and electronics industries as alloying agent due to its excellent catalytic activity.⁹⁻¹¹ If added in Ti and other super alloys such as those applied in aerospace industry, Ru improved the corrosion resistance as well as chemical and electrical stability at higher temperatures.^{12,13}

Common to all PGMs is that they form a B2 (austenite) phase with Ti at high temperature and at compositions closer to 50:50 atomic percent (at.%). For most PGMs, the B2 phase transforms in a diffusionless manner (martensitically) on cooling to orthorhombic or

tetragonal intermetallic phases.^{14,15} This martensitic transformation is one of the key characteristics for shape memory behaviour, which makes them potential materials for high temperature shape memory alloys (HTSMAs) if it occurs above 100°C, earmarked for possible application in aerospace engines. However, only the phase stability of B2 TiRu phase is maintained to room temperature, hence it is not listed among PGM-based potential HTSMA materials despite its cost benefits.^{10,11,16} This highly stable B2 phase behaviour is also found in other transition metals belonging to group VIII of the periodic table of elements.¹⁶⁻¹⁹

Upon comprehensive study of the Ti-Ru system, Murray²⁰ reported that the equiatomic TiRu binary compound crystallizes in the B2-type crystal structure with space group Pm-3m of an ordered body centered cubic (BCC) CsCl-type.^{17,18,21} This B2 phase is a sole high temperature intermetallic phase of the TiRu system with lattice parameter ranging from 3.06 to 3.076 Å, and it undergoes congruent melting at 2130°C. CsCl-type titanium intermetallic compounds are currently the most attractive hydrogen storage materials.²² Experimental work at MINTEK on the equiatomic TiRu alloy found that this B2 phase is brittle.²³

The TiPd binary alloys have been widely used in severe, corrosive services in the chemical process industries.²⁴ Moreover, there is a strong interest in TiPd alloys due to their interesting mechanical properties and technological importance for engineering and medicine, in particular for the shape memory effect and for the property of reversible hydrogen storage.²⁵ However, with the market price of Pd metal has been rising over the past few years,¹¹ which renders Pd selection for such industries unattractive. One of the noted reasons hampering the industrial use of PGM based

Ti SMAs is the high cost, therefore the focus of this work was on finding a relatively cheaper alternative alloy. The systematic introduction of up to 25 at.%Pd on the Ru site is aimed to reduce the stability of B2 TiRu phase to the point where this B2 phase transform to a lower temperature phase such as B19 orthorhombic (found in TiAu, TiPd and TiPt), B19' monoclinic (found in NiTi) or L1₀ tetragonal (found in IrTi) accompanied by shape memory effects (SME).^{14,15,26-28}

This work also observed the atomistic and the *ab initio* modelling work carried out by other researchers while acknowledging that there is still limited literature available on equiatomic Ti-Ru^{10,16,20,21,29,30} and ternary Ti-Pd-Ru alloys.²⁹ Diale et al.²⁹ employed supercell (SC) approach to study the effect of Ru on B2 Ti₅₀Pd₅₀ with a composition change of 6.25 at. % steps using VASP. It is well known that shape memory behaviour is very sensitive to composition change,³¹ hence the current choice of approach that allows smaller composition variations.

In this work, a density functional theory based on virtual crystal approximation (VCA) solid-solution unit cell approach is used to investigate the Pd alloying effect on phase stability and elastic properties of the ordered B2 equiatomic TiRu phase with smaller composition changes of 2.5 at. % steps^{28,32} to represent B2 (1-x) TiRu-(x) TiPd solid solutions. This approach was carried out with the objective to induce martensitic transformation in a stable B2 TiRu phase.

2. Methodology

The calculations were performed using DFT - based plane-waves pseudopotential code CASTEP as implemented in Materials Studio software,³³ with the projector augmented wave (PAW).³⁴ The electron-exchange and correlation were described by the Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA).³⁵ An energy cut-off of 500eV, and k-points of 13×13×13 were used, and were found to be sufficient to converge the total energy of the B2 Ti₅₀Ru_{50-x}Pd_x alloys with x ranging from 0, 2.5, 5, 7.5, 10, 15, 25 and 50 at. %.

All the equilibrium crystal structures were obtained via geometry optimization in the Brayden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme.³⁶ The convergence criterion of less than 1×10⁻⁵ eV/atom, the maximum residual forces of 0.03 eV/Å, maximum residual bulk stress of 0.05GPa and maximum atomic displacement of 1×10⁻³ Å were utilized to achieve reasonable accuracy. The elastic constants were computed from optimized crystal structure for each composition.

2.1 Phase stability

The stability of any compound can be deduced from the heats of formation commonly known as enthalpy of formation H_f ³⁷ and it is used to determine the thermodynamic stability of phases. A phase is thermodynamically stable if H_f is found to be negative, else the phase becomes less thermodynamically stable if less negative or unstable if found to be positive.³⁸ This stability property is expressed in Equation 1,

$$H_f = \left\{ \frac{1}{2} E_{Tot}^{Ti_{50}Ru_{50-x}Pd_x} - x E_{Solid}^{Ti} - (1-x) E_{Solid}^{Ru_{50-x}Pd_x} \right\} \quad (1)$$

where, $E_{Tot}^{Ti_{50}Ru_{50-x}Pd_x}$ is the calculated total energy of the intermetallic phase, E_{Solid}^{Ti} and $E_{Solid}^{Ru_{50-x}Pd_x}$ are total energies of the pure elements or solid-solutions in their stable ground-state crystal structures, respectively, while x and $(1-x)$ refer to the fractional composition of the constituent elements.

2.2 Elastic and mechanical properties

Elastic constants of solid materials provide a link between the mechanical and dynamical behaviour of crystals, and give important information about bonding characteristics at the equilibrium state.^{39,40} Other physical properties such as anisotropy factor, hardness, ductility and other important mechanical properties can be calculated from the elastic constants. The elastic stiffness constants (ij=1, 2, 3, 4, 5 and 6), forming a 6×6 symmetric tensor matrix, determine the response of the strain to external forces that can be obtained by applying a set of finite homogeneous deformations to a unit cell and by optimizing the internal atomic freedoms to calculate the stresses.⁴¹ B2 is a cubic system consisting of the simplest form of a stiffness matrix, where the number of independent elastic constants are reduced to three (C_{11} , C_{12} and C_{44}) in the Voigt notation, and the expression for shear elastic constants C' is shown in Equation 2.

$$C' = \frac{C_{11} - C_{12}}{2} \quad (2)$$

According to Born-Huang's lattice dynamical theory,^{42,43} the mechanical stability criteria for B2 cubic crystals can be determined by satisfying the criteria given by a set of expressions in Equation 3.

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0. \quad (3)$$

The crystal mechanical stability decreases when approaching the martensitic transition temperature, where the tetragonal shear modulus (C') becomes much smaller than the monoclinic shear constant (C_{44}) which represents the stiffness of the crystal against shear.⁴⁴ The Zener anisotropic factor (A) is given as the ratio of C_{44} to C' and it is equal to 1 for isotropic crystals. Some of the mechanical properties determined from the computed elastic constants include the bulk modulus (B), trigonal shear modulus (G), Young's modulus (E) and the Poisson's ratio (ν).^{10,16,21,29,30} In all crystal structures, the polycrystalline elastic modulus can be estimated from their set of independent elastic constants by two approximation methods, *i.e.* the Voigt (V) method which is the upper bound and the Reuss (R) method which is the lower bound as shown by a set of expressions given in Equation 4 for cubic crystal structures.

$$B_V = B_R = \frac{1}{3}(C_{11} + 2C_{12}), G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \text{ and } G_R = \frac{(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}. \quad (4)$$

The arithmetic average of the Voigt and Reuss is called the Voigt-Reuss-Hill (VHR) average. Thus the average shear (G_H) and bulk (B_H) modulus can be calculated using the set of expressions in Equation 5, including the average Young's modulus (E) and the Poisson's ratio (ν) of the polycrystalline materials:

$$G_H = \frac{G_V - G_R}{2}, B_H = \frac{B_V - B_R}{2}, E = \frac{9B_H G_H}{3B_H + G_H} \text{ and } \nu = 0.5 \left(\frac{3B_H - 2G_H}{3B_H + G_H} \right). \quad (5)$$

The relationship between the interatomic bonding and the physical properties can be considered using Pugh's (B/G) and Poisson's (ν) ratios. Pugh's ratio which is used to describe the brittleness and ductility of metals, while the hardness is defined as the resistance of a material to external mechanical pressure. Vickers hardness (H_V) is usually used in first-principles calculations⁴⁵ to measure the resistance of solids to plastic or permanent deformation. The expression employed to determine the H_V is shown in Equation 6.

$$H_V = 0.92(k)^{1.137} \times G^{0.708}, \quad (6)$$

where, $k = \frac{G}{B}$ is the inverse of Pugh's modulus ratio.

The first-principles calculations are considered as novel method for micro-investigation at the atomic scale to study the physical properties of solids.

2.3 Electronic properties

The study of electronic structures through the density of states (DOS) provides insights about the formation of alloys, and their phase stability.⁴⁶ The DOS of a system describes how dense the states are populated per energy level.⁴⁷ A DOS of zero at Fermi level (E_F) means that the states are empty, rendering the material an insulator⁴⁸ due to the unavailability of electrons in the conduction band. In intermetallic compounds, there exists a pseudogap at the Fermi level (E_F) of the DOS spectra that determines the stability of the compound. If the constituent metals are able to form an ordered intermetallic phase which is stable at low temperature, the E_F falls at the centre of the pseudogap, whereas if the ordered phase forms but is only stable at high temperature then the E_F cuts on the shoulder of the DOS peak, indicating instability of the phase at 0 K. Thus high DOS at E_F is considered to be related to the structural instability.⁴⁹ And taking into account that at the anti-bonding region the DOS values are higher, the phase having high transition temperature will undergo structural reconfiguration to minimize the higher energy indicated by $N(E_F)$. Consequently, those systems with higher energy in the anti-bonding region will undergo MT and hence have potential to exhibit the SME.

Thus, the electronic properties of the investigated alloys were determined from the TDOS spectra obtained from the optimised structures in terms of stability. They were also compared with those of TiPd and TiNi that are well known to possess the SME.^{17,18}

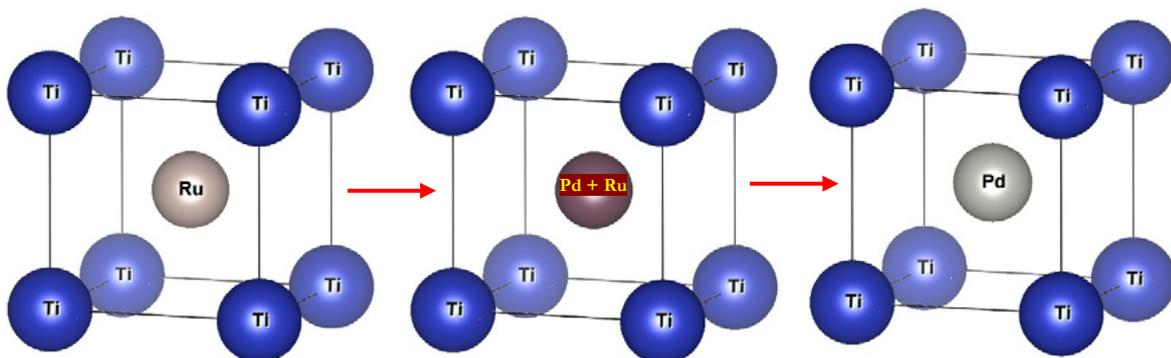


Figure 1: Crystal structure models of B2 TiRu, $\text{Ti}_{50}\text{-Ru}_{50-x}\text{-Pd}_x$ and TiPd compositions used in the calculations

3. Results and discussion

3.1 Structural properties and enthalpies of formation

The B2 cubic crystal structures of TiRu, $\text{Ti}_{50}\text{Ru}_{50-x}\text{Pd}_x$ and TiPd used in this work are shown in Fig. 1, while the obtained equilibrium lattice parameters of the investigated alloys as well as their corresponding calculated enthalpies of formation are presented in Table 1. As shown in Table 1, the predicted lattice parameters of pure and alloyed B2 phases were found to be within the acceptable error margin of 3% and in agreement with previous works.^{10,23,25,29,50} The lattice parameter of the investigated ternaries ($\text{Ti}_{50}\text{Ru}_{50-x}\text{Pd}_x$) slightly increases with Pd addition. This is expected since Pd atom has a larger atomic radius than Ru atom.

The calculated H_f show that the B2 TiRu phase is the most thermodynamically stable compared to TiPd and TiNi, with TiNi found to be the least stable. These values were compared with available data and found to be in good agreement.¹⁶ It is interesting to note that heat of formation for B2 $\text{Ti}_{50}\text{Ru}_{50-x}\text{Pd}_x$ increased with addition of ≤ 7.5 at.% Pd, but at Pd composition above 7.5 at.% decreased H_f signifying reduced stability. The observation at Pd ≤ 7.5 at. % is in contrast to that of Diale et al, whereas at Pd > 7.5 at.% is in agreement, though their results show a strong linear trend.²⁹

Table 1: Optimised structural models and formation enthalpies of the investigated B2 alloys

Phases	Lattice Parameters, a(Å)			ΔH_f (eV/atom)	
	GGA	Literature	V(Å ³)	GGA	Literature
TiNi	3.059	3.015	28.62	-0.351	-
TiRu	3.097	3.087 ^{10,21}	29.7	-0.819	0.743 ¹⁶
$\text{Ti}_{50}\text{Ru}_{47.5}\text{Pd}_{2.5}$	3.097	-	29.71	-0.853	-
$\text{Ti}_{50}\text{Ru}_{45}\text{Pd}_5$	3.099	-	29.75	-0.837	-
$\text{Ti}_{50}\text{Ru}_{42.5}\text{Pd}_{7.5}$	3.101	-	29.84	-0.82	-
$\text{Ti}_{50}\text{Ru}_{40}\text{Pd}_{10}$	3.104	-	29.92	-0.802	-
$\text{Ti}_{50}\text{Ru}_{35}\text{Pd}_{15}$	3.114	-	30.19	-0.765	-
$\text{Ti}_{50}\text{Ru}_{25}\text{Pd}_{25}$	3.151	-	31.29	-0.725	-
TiPd	3.227	3.17 ²⁹	33.6	-0.373	0.519 ^{16,25}

3.2 Elastic constants and mechanical properties

The calculated elastic constants and deduced elastic moduli results of the investigated alloys are presented in Fig. 2. Fig. 2(a) shows

that the calculated elastic constants of B2 TiRu met the mechanical stability criterion set in Equation 3 for cubic crystals. However, this criteria was not satisfied for B2 TiPd, which indicates its mechanical instability at 0 K. Substituting some Ru atoms with Pd in pure TiRu, gradually decreased C_{11} and C_{44} while, C_{12} and C_p increased up to 15 at.% Pd. It is between 10 and 15 at.%, where the mechanical stability criteria was broken ($C_{11} < C_{12}$), and rendered the B2 phases unstable, which could be associated with a potential martensitic transition of a lower temperature phase with possibility of SME. Pettifor et al.^{39,51} stated that materials with metallic bonds become ductile if it has larger positive Cauchy pressure (C_p), suggesting that the predicted ternary compositions would be more ductile than pure B2 TiRu. The metallicity of the B2 TiRu was found to strongly increase when more Pd atoms substitute Ru atoms and the $Ti_{50}Ru_{35}Pd_{15}$ alloy had the highest metallic bonding and hence most ductility as indicated by the highest C_p amongst the investigated alloys.

The elastic modulus properties such as B , G , E and H_v are important in determining the strength of materials, and these results are shown in Fig. 2(b). The G , E and H_v decreased significantly, while B decreased gradually on adding up to 15 at. % Pd, and above this composition, E and H_v remained almost constant whereas B dropped significantly.

Jain et al.,¹⁰ stated that higher Young's modulus (E) is associated with covalent or ionic bonds. Therefore, the larger E the harder the material to deform, whereas the smaller E the easier the materials to deform. The pure TiRu phase was found to have a higher value of E (316.2GPa) indicating rigidity, while the $Ti_{50}Ru_{25}Pd_{25}$ had the

lowest E amongst the investigated ternary compositions. Therefore, these compositions are expected to deform plastically, resulting in lower hardness as predicted. In many cases, the compound with high H_v has large G , indicating that the hardness of materials is more sensitive to shear modulus than to bulk modulus.^{40,52}

To further characterize the ductility of the crystal structures, the Pugh's and Poisson's ratios were also evaluated. The determined Poisson's ratio ν , the classical Pugh's modulus ratio B/G , tetragonal shear modulus (C') and elastic anisotropy (A) of the investigated compositions are presented in Fig. 3. The A , ν and B/G increased with increased Pd while shear modulus C' and H_v decreased, at least up to 15 at.%.

The results obtained showed that addition of Pd yielded some ductility to B2 TiRu. These results predict that at Pd compositions just above 10 at. %, the B2 phase becomes mechanically unstable as opposed to above 25 at. % as predicted by Diale et al.²⁹ The $Ti_{50}Ru_{50-x}Pd_x$ ternary compositions were found to be ductile, since their B/G was above 1.75 threshold value.^{53,54} Although the Pugh's ratio of TiRu was in compliance with Pugh's criteria for ductility, it is suggested for the first time here that a new factor be considered to predict increased ductility of B2 cubic crystals: the ratio of trigonal shear modulus (G) to tetragonal shear moduli (C'). For easy plastic shearing to occur G/C' must be greater than 1, and in this work, this criteria was satisfied in alloys containing ≥ 10 at. % Pd. It is likely that this particular shearing criterion is responsible for martensitic transformation in known B2 Ti-X shape memory alloys.

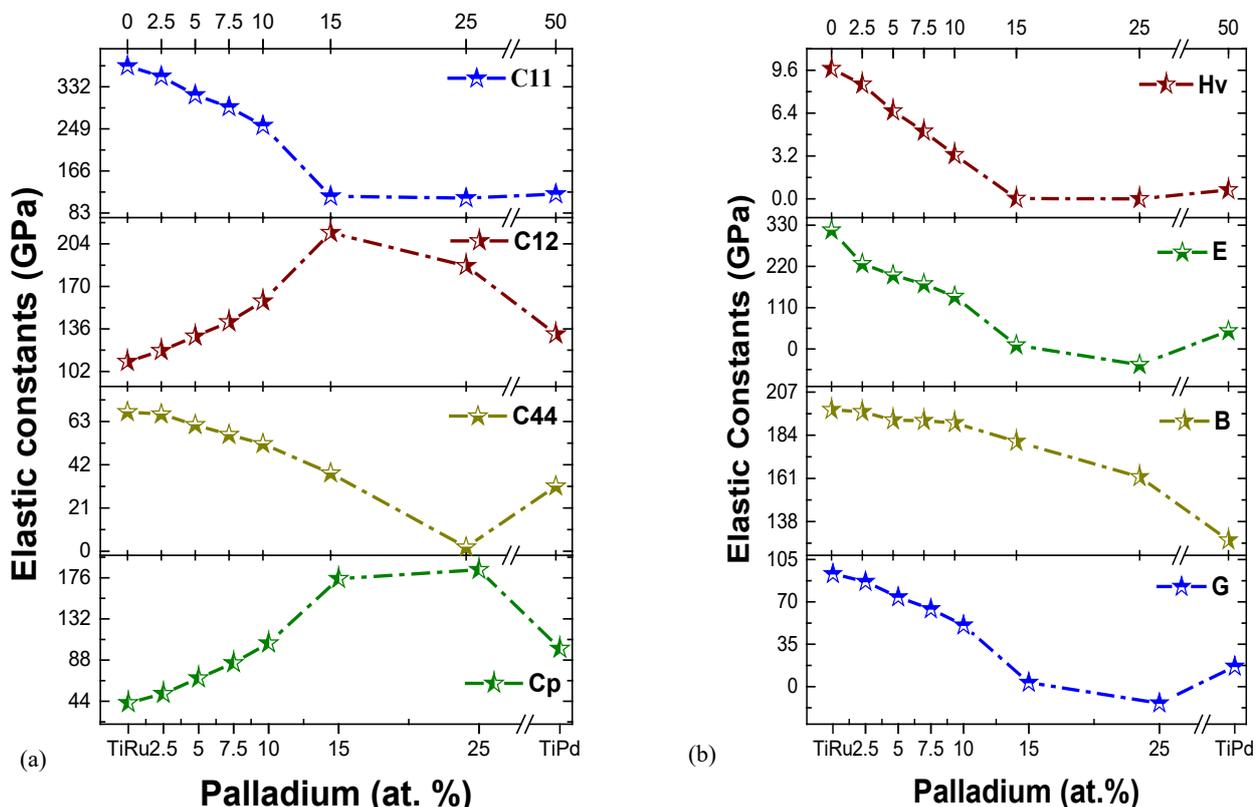


Figure 2: Cubic crystal independence elastic constants C_{11} , C_{12} , C_{44} , C_p and the elastic modulus of the investigated B2 $Ti_{50}Ru_{50-x}Pd_x$ compositions

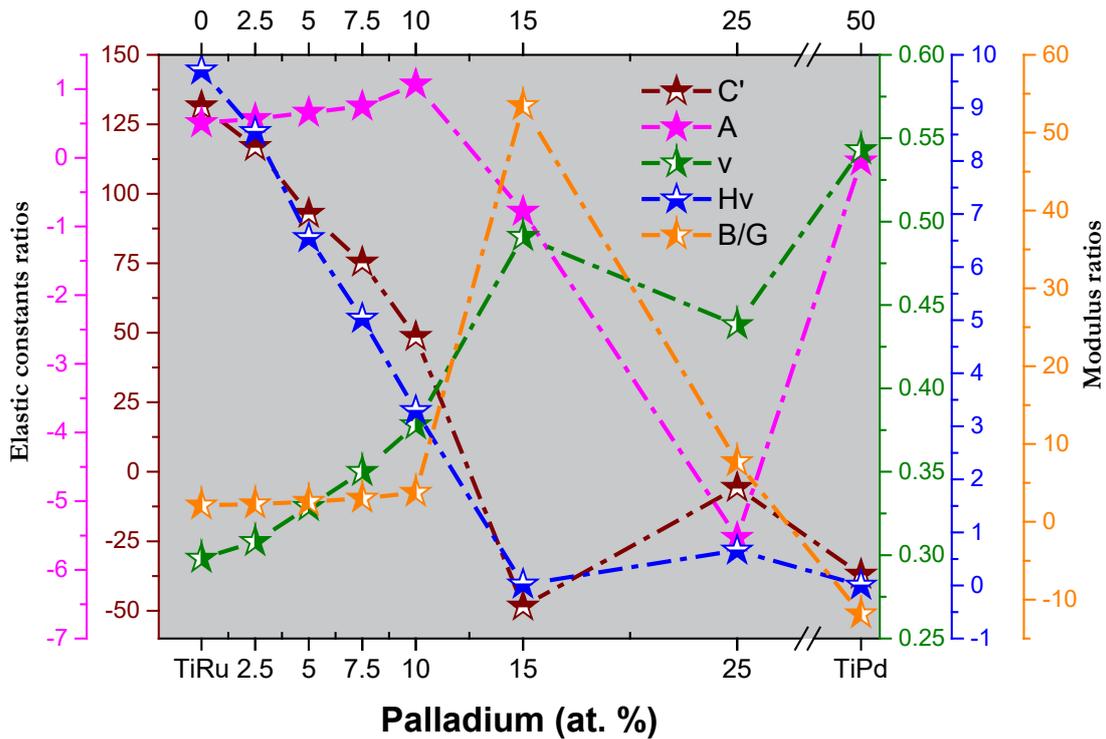


Figure 3: Elastic moduli ratios, shear modulus C' and corresponding H_v of the investigated B2 compositions

In addition, Frantsevich’s rule states that the ductility or brittleness of a material can also be determined in terms of its Poisson ratio (ν), and provides information about the bonding of materials.⁵⁵ Frantsevich’s rule suggests that if ν is closer to $1/3$, the material will be ductile (consist of metallic bonds), otherwise the material will be brittle (consist of covalent or ionic bonds) with ratios much smaller than $1/3$.^{48,54,55} Fig. 3 shows that the calculated ν for the ternary compositions were more ductile as they possess stronger metallic bonds, having $\nu > 0.333$. The ordered TiRu was expected to possess some covalent bond characteristics with its $\nu < 0.298$.

3.3 Electronic properties

The electronic structure and chemical bonding characteristics of the investigated B2 $Ti_{50}Ru_{50-x}Pd_x$ compositions are presented in

Fig. 4 with those of B2 TiNi and TiPd for comparison. The total densities of states (TDOS) for the investigated alloys were non-zero across the Fermi level (E_F), indicating that the plain B2 TiRu and B2 $Ti_{50}Ru_{50-x}Pd_x$ compositions were mainly characterised by metallic bonds. The TDOS values at E_F were 0.52, 1.17, 1.66, 1.23, 1.25, 3.18, 3.40, 2.25 and 2.15/eV for Pd compositions ranging from 0, 2.5, 5, 7.5, 10, 15, 25, 50 at. % and TiNi, respectively. Again, the $Ti_{50}Ru_{35}Pd_{15}$ composition had the highest metallicity, correlating to the highest B/G and C_p .

Fig. 4 shows that the conduction and valence band coincide perfectly, resulting in a deep valley around the Fermi level of TDOS for B2 TiRu, signifying that this phase is thermodynamically stable at 0K and without a phase transformation. Thus, B2 TiRu does not

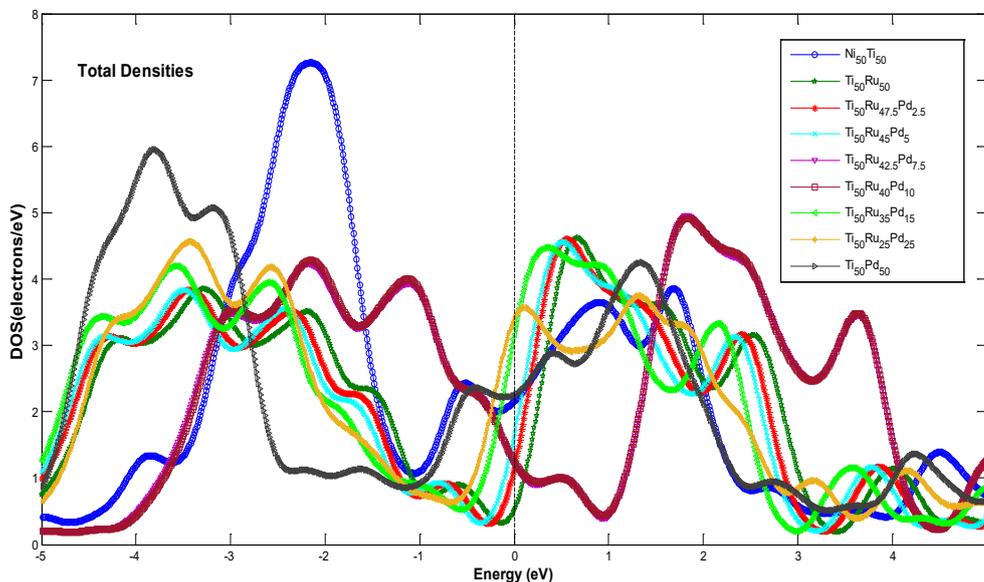


Figure 4: Total densities (TDOS) of B2 TiNi and $Ti_{50}Ru_{50-x}Pd_x$ ($x = 0, 2.5, 5, 7.5, 10, 15, 25$ and 50 at. %) compositions

exhibit SME at room temperature, since SMAs usually show E_F cutting on the shoulder of TDOS curve above the pseudogap.⁵⁶ However, introducing Pd on Ru site, shifted the deep-valley towards the conduction band with E_F cutting on the shoulder of TDOS curve. This indicates that adding Pd induces instability in B2 TiRu, enabling it to potentially exhibit the SME and hence be considered as a potential SMA, in agreement with the previous study.²⁹ Furthermore, the higher DOS values seem to signal higher transition temperature as can be seen in B2 TiPd, with high possibility to undergo MT and subsequently exhibit SME.

4. Conclusions

For ternary compositions above 10 at.% Pd, the mechanical stability criteria is broken ($C_{11} < C_{12}$), rendering the B2 phase unstable, which can be associated with a potential martensitic transition to a lower temperature phase, with the possibility to possess SME. This study proposes for the first time a new factor to be taken into consideration when predicting increased ductility of B2 cubic crystals: the ratio of trigonal shear modulus (G) to tetragonal shear moduli (C') to be greater than 1. In agreement with mechanical stability predictions, the DOS results also revealed that adding Pd induced instability in B2 TiRu, suggesting that these alloys could be considered as potential SMAs with SME.

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Contribution

The authors contributed equally on project initiation with BSN carrying out calculations under MJP supervision. Both were equally involved in interpretation of results. IAM's contribution was mainly on the overall project scope and direction.

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