Chapter

Titanium Aluminide Coating: Structural and Elastic Properties by DFT Approach

Ouahiba Ouadah

Abstract

The stability, elastic and electronic properties of titanium aluminide compounds have been systematically studied by the first-principles calculation. The calculated lattice parameters are consistent with the results found in the literature. The three Ti-Al binary compounds are thermodynamically stable intermetallics depending on their negative formation enthalpy. It has been found that the Ti-Al binary compounds are composed of both metallic and covalent bonds. Elastic properties revealed that these alloys are more resistant to deformation along *the a-* and *c-axis*. Besides, the (001)[100] deformation would be easier than (010)[100] deformation for these alloys. The results found in this chapter give a reliable reference for the design of novel Ti-Al binary alloys.

Keywords: Titanium aluminide, elastic properties, stability, first-principles calculation

1. Introduction

Titanium aluminide-based alloys (TiAl) have attracted more attention as a potential coating material for high-temperature structural applications. They have many applications in engineering due to their high melting points, high tensile strength, good stiffness, low density, high corrosion, and oxidation resistance at elevated temperature [1–3]. TiAl has an ordered tetragonal face-centered γ-TiAl phase and a hexagonal α_2 (Ti_3Al) phase DO_{19}. Experimental works highlighted that the deformation mechanism ($\alpha_2 + \gamma$) binary phase is mainly made by ordinary dislocation, super-dislocations, and twinning following the compact plane (111) [4–6]. However, TiAl intermetallic compounds suffer from low ductility and toughness at room temperature, which seriously limits their broad range of applications [7].

To understand the bonding and materials characteristics of this type of system, many experimental and theoretical studies have been investigated. A study of fundamental properties such as the nature of interatomic bonding, the stability of crystal structures, elastic properties, dislocations, grain boundaries, interfaces, as well as point defects and diffusion are therefore warranted to gain more insight into the behavior of these intermetallic alloys under high temperatures [8]. Sun et al. [9] have synthesized a new multilayer TiAl intermetallic by spark plasma sintering, which provides a novel possibility to improve fracture toughness. It is believed that TiAl intermetallic compounds with different Al contents play important roles in controlling the microstructure and mechanical properties.

Several ab-initio studies of the structural stability, elastic properties, and the nature of bonding have been reported for γ-TiAl, α_2-Ti_3Al, and B2-TiAl [10–13]. To optimize ion beam treatment of TiAl based intermetallic alloys for better performance. It is essential to gain a deeper insight into radiation effects in these materials. From the fundamental perspective, TiAl intermetallic compounds represent a good model system for studying radiation effects in ordered metallic alloys for future engineering applications. To understand some of the physical properties of these compounds, knowledge of the phase stability and elastic properties of TiAl binary compounds is required. In this chapter, we summarized the calculated results of TiAl intermetallic compounds using density functional density (DFT).

2. Computational details

Ab initio calculation is a useful method to predict and explore the interrelationships among structure properties. In this chapter, the first-principles modeling

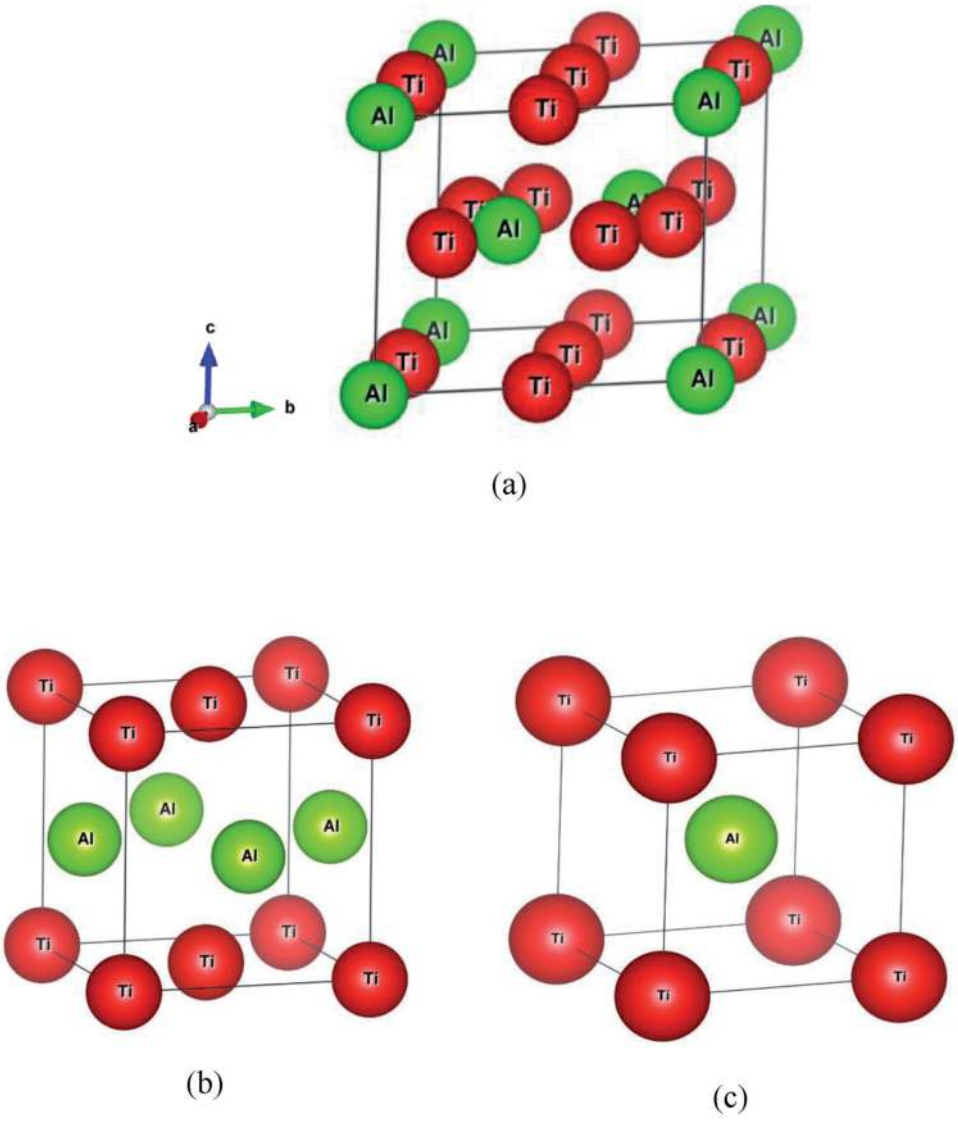

Figure 1.
Crystal structures of titanium aluminides. (a) DO19, (b) L10, and (c) B2.

based on the density functional theory (DFT) was implemented in the Vienna Ab-initio Software Package (VASP) [14, 15]. Projector Augmented Wave (PAW) [16] pseudopotential is used to describe the interactions between electrons and ions [17]. The exchange and correlation energy have been performed using the Generalized Gradient Approximation (GGA) [18]. Plane-wave cutoff energy of 400 eV was used for all calculations. In this work, the k-point method has been adopted for sampling the Brillouin zone and selected to 18 x 18 x 18. The Brillouin zone integration was executed using the Methfessel-Paxton technique [19] with a 0.1 eV smearing of the electron levels. The fully structural relaxations were performed by minimizing the ionic Hellman-Feynman [20] force until the maximum forces achieved less than 0.02 eV.

Titanium aluminides crystallized in three major phases: Hexagonal Ti_3Al, cubic TiAl, and tetragonal TiAl, as shown in **Figure 1**.

3. Structural properties

The total energy of TiAl and Ti_3Al intermetallic compounds was calculated at many different volumes around equilibrium fitted to Murnaghan's equation of state from which we obtained the equilibrium structural parameters. The computed equilibrium lattice parameters and the bulk modulus of these compounds are listed in **Table 1**. The calculated lattice parameters and the bulk modulus (B) for these compounds are in good agreement with those measured experimentally. Hence, we can see that the computation parameters and conditions selected in the present work should be suitable.

To examine the stability of these systems, the formation enthalpy (ΔH) was calculated by

$$\Delta H = E_{total}(TiAl) - E_{solid}(Ti) - E_{solid}(Al) \quad (1)$$

We can see that the enthalpies of formation E_f of this compound crystallizing in the three phases take negative values. This indicated that the three phases of titanium aluminide are energetically stable. From these values, we can see that all three phases can exist with the γ-TiAl phase as the most energetically stable. These findings are in good agreement with the previous published works [21–28].

	a (Å)	**c (Å)**	**c/a**	**B_0 (GPa)**	**B′**	**ΔE_f (eV/at.)**
B2-TiAl	3.185 *3.189* [21] *3.196* [22]	—	—	111.46	4.04	−0.265
γ-TiAl	3.993 *3.997* [23] *3.996* [24]	4.068 *4.062* [23] *4.075* [24]	1.018 *1.016* [23] *1.020* [24]	113.88 *113.29* [23] *112.82* [24]	3.95 *3.76* [24]	−0.405 *-0.367* [25]
α_2-Ti_3Al	5.746 *5.765* [26] *5.760* [27]	4.666 *4.625* [26] *4.659* [27]	0.812 *0.802* [26] *0.809* [27]	114.81 *113* [26] *114.39* [27]	3.83 *3.61* [27]	−0.275 *-0.290* [28]

Table 1.
Lattice parameters, bulk modulus, and formation enthalpy for B2-TiAl, γ-TiAl, and α_2-Ti_3Al compounds.

4. Elastic properties

Knowledge of elastic constants provides more information about mechanical properties and understanding of the usefulness of the materials. Mechanical stability requires that its independent elastic constants should satisfy the following Born's stability criteria.

For a tetragonal crystal

$$C_{44} > 0, C_{66} > 0, C_{11} > |C_{12}|, \ (C_{11} + C_{12}) C_{33} > 2 C^2_{13} \tag{2}$$

For a hexagonal crystal

$$C_{44} > 0; C_{11} - |C_{12}| > 0; (C_{11} + 2C_{12}) C_{33} - 2 C^2_{13} > 0 \tag{3}$$

For a cubic structure

$$C_{11} + 2 C_{12} > 0; \quad C_{11} - C_{12} > 0; C_{44} > 0 \tag{4}$$

According to the symmetry of crystalline systems, some elastic constants are null. In this part, **Table 2** gives an overview of the expression of the stiffness tensors corresponding to each crystal system studied (cubic, hexagonal and tetragonal). The cubic structure has the simplest elastic matrix, with only 3 independent

Crystal System	**Point symmetry group**	**Stiffness Tensor**
Cubic	23 m-3 432 -43 m m-3 m	$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ & C_{11} & C_{12} & 0 & 0 & 0 \\ & & C_{11} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{44} \end{pmatrix}$
Hexagonal	6 −6 6/m 622 6 mm -62 m 6/mmm	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix}$
Tetragonal	422 4 mm −42 m 4/mmm 4 -4 4/m	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix}$

Table 2.
The stiffness tensors of the elastic constants corresponding to the systems: cubic, hexagonal and tetragonal.

	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{66} (GPa)
B2-TiAl	76.04	118.26	—	—	71.98	—
γ-TiAl	179.20	94.90	84.63	167.96	113.84	72.12
	183 [29]	*74.1* [29]	*74.4* [29]	*178* [29]	*105* [29]	*78.4* [29]
	173 [24]	*83* [24]	*84* [24]	*168* [24]	*111* [24]	*75* [24]
α_2-Ti_3Al	217.36	98.75	78.23	237.27	59.30	--
	175 [30]	*88.7* [30]	*62.3* [30]	*220* [30]	*62.2* [30]	--
	185 [31]	*83* [31]	*63* [31]	*231* [31]	*57* [31]	--

Table 3.
Elastic constants for B2-TiAl, γ-TiAl and α_2-Ti_3Al compounds.

constants, while the elastic matrices of the hexagonal and tetragonal structures have five and six constants respectively.

Table 3 clearly shows that all elastic constants satisfy well the required stability conditions, indicating that both TiAl and Ti_3Al compounds are mechanically stable. In addition, our elastic constants calculated fit the experimental and theoretical values. As known, the elastic constants C_{11} and C_{33} measure the resistance of alloys under uniaxial stress along *a*- and *c-axis*. The results obtained allow us to predict that these alloys are more resistant to deformation along a and c-axis. Moreover, the C_{66} value is significantly lower than C_{44} suggesting; thus, that the (001)[100] deformation would be easier than (010)[100] deformation for these alloys. On the other hand, we can see that the elastic constants of B2 structure do not required the Born-Huang's stability criteria. This indicates that B2-TiAl phase is mechanically unstable, although it is energetically stable as mentioned above.

5. Electronic properties

It is well-known that the physical properties of a material are strongly correlated to its electronic structure nature. So, by applying the obtained equilibrium structural parameters, the total and partial densities of states (TDOS and PDOS) were calculated along the principal symmetry directions in the Brillouin zone to further understand the reasonable relationship between the mechanical behavior and bonding characteristics of γ-TiAl based alloys. The total and partial DOS of pure $L1_0$-TiAl, α_2-Ti_3Al, and B2-TiAl compounds are depicted in **Figure 2**.

We can see that Ti-DOS typically Ti-d states play a very important role in the total density of TiAl in $L1_0$ structure. In this compound, the total state density has two regions in the valence band: a deep region dominated by Al-s states, the second one is constituted by Al-p and Ti-d states, which are separated by a strong hybridization where Al-p states forming a peak at about −1.5 eV which is more localized contributes to the strong covalence in Ti-d-Al-p bonds. Al the Fermi level, the density of states is not zero, dominated mainly by Ti-d states, attesting to the weak metallic character of this intermetallic class. Hence, the interactions of the strong covalent bond with the weak metallic bond cause an unequal distribution of these forces leading to a cleavage fracture in the direction of the metallic interactions.

From **Figure 2**, the interactions between Al-3p and 3d-Ti take place in the Ti-Al binary compounds, leading to the enhancement of the covalent bonding. By the way, it can be found that Al-3p plays an important role in the pseudogap of Ti-Al compound.

Through the further analysis of PDOS, the peaks of the PDOS of Ti-3d and Al-3p are exactly overlapped, indicating the strong covalent bonding originates

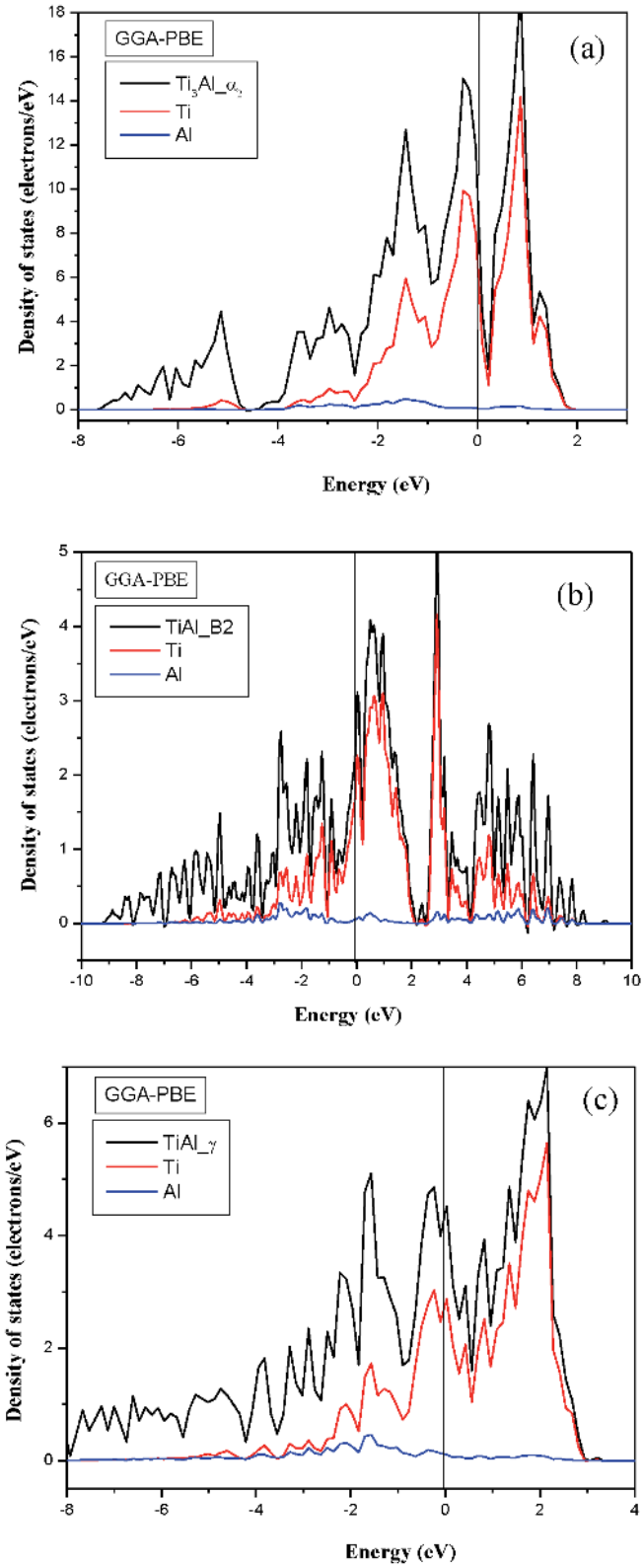

Figure 2.
The total and partial density of states (DOS) for: (a) α_2-Ti_3Al, (b) B2-TiAl, (c) γ-TiAl.

from the interaction between Ti-3d and Al-3p. Sometimes, a high DOS value at Fermi level means unstable structures in some degree. In this work, the values of total DOS at Fermi level of Ti_3Al, B2-TiAl, and γ-TiAl compounds are 10.8 eV, 3.4 eV,

and 3.0 eV, respectively. From this point of view, Ti_3Al compound is considered to be the least stable Ti-Al binary compound.

6. Conclusion

In this chapter, we have studied the structural, elastic, and electronic properties of titanium aluminide intermetallic compounds using first-principles calculations based on density functional theory (DFT). The use of the GGA-PBE approximation for the exchanging correlation potential allowed us to obtain good results of the electronic structure. B2-TiAl, γ-TiAl, and α_2-Ti_3Al are thermodynamically stable according to both thermodynamical and mechanical criteria. Whereas, B2-TiAl compound is mechanically unstable. Besides, elastic properties showed that these alloys are more resistant to deformation along *a-* and *c-axis*. Moreover, the C_{66} value is significantly lower than C_{44} suggesting; thus, that the (001)[100] deformation would be easier than (010)[100] deformation for these alloys. Based on the electronic structure, titanium aluminide binary compounds are composed of both metallic bonds and covalent bonds. α_2-Ti_3Al shows the strongest metallic bonding character.

Conflict of interest

The authors declare no conflict of interest.

Author details

Ouahiba Ouadah
Division of Materials Discovery (DEPM), Unit of Research of Materials and Renewable Energies (URMER), University Abou Bekr Belkaid, Tlemcen, Algeria

*Address all correspondence to: ouahiba.ouadah@univ-tlemcen.dz

References

[1] Zope R.R and Mishin Y, Interatomic potentials for atomistic simulations of the Ti-Al system, Phys. Rev. B. 2003, 68: 024102. DOI: https://doi.org/10.1103/PhysRevB.68.024102

[2] Nui H.Z, Chen Y.Y, Xiao S.L. Xu, Microstructure evolution and mechanical properties of a novel beta γ-TiAl alloy, Intermetallics, 2012, 31: 225-231. DOI: 10.1016/j.intermet.2012.07.012

[3] Ouadah O, Merad G, Si Abdelkader H, Atomistic modeling of γ-TiAl/α_2-Ti_3Al interfacial properties affected by solutes, Mater. Chem. Phys. 2021; 257: 123434. DOI: 10.1016/j.matchemphys.2020.123434

[4] Appel F, Paul J.D.H, Oehring M, Gamma Titanium Aluminide Alloys: Science and technology. 1st ed. VCH, Weinheim: Wiley; 2011. DOI. 10.1002/9783527636204

[5] Appel F, Clemens H, Fischer F.D, Modeling concepts for intermetallic titanium aluminides. Prog. Mater. Sci. 2016; 81: 55-124. DOI: 10.1016/j.pmatsci.2016.01.001

[6] Kanani M, Hartmaier A, Janisch R, Interface properties in lamellar TiAl microstructures from density functional theory, 2014; 54: 154-163. DOI: https://doi.org/10.1016/j.intermet.2014.06.001

[7] Parrini L, Influence of the temperature on the plastic deformation in TiAl, 1999; 30: 2865-2873. DOI: 10.1007/s11661-999-0124-7

[8] Wen Y.F, Sun J, Generalized planar fault energies and mechanical twinning in gamma TiAl alloys, 2013; 68: 759-762. DOI: 10.1016/j.scriptamat.2012.12.032

[9] Sun Y, Vajpai S.K, Ameyama K, Ma C, Fabrication of multilayered Ti-Al intermetallics by spark plasma sintering, 2014; 585: 734-740. DOI: 10.1016/j.jallcom.2013.09.215

[10] Ouadah O, Merad G, Si Abdelkader H, Theoretic quantum analysis of mechanical and electronic properties of TiAl-M (M= Mo, W, Cu and Zn), Int. J. Quantum Chem. 2020;e26590. DOI: 10.1002/qua.26590

[11] Jian Y, Huang Y, Xing J, Sun L, Lui Y, Gao P, Phase stability, mechanical properties and electronic structures of Ti-Al binary compounds by first principles calculations, Mater. Chem. Phys. 2019; 221: 311-321. DOI: 10.1016/j.matchemphys.2018.09.055

[12] Dumitraschkewitz P, Clemens H, Mayer S, Holec D, Impact of alloying on stacking fault energies in γ-TiAl, Appl. Sci. 2017; 7: 1193. DOI: 10.3390/app7111193

[13] Lui Y.L, Lui L.M, Wang S.Q, Ye H.Q, First-principles study of shear deformation in TiAl and Ti_3Al, Intermetallics. 2007; 15: 428-435. DOI: 10.1016/j.intermet.2006.08.012

[14] Kresse G, Furthmüller J, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 1996; 6: 15. DOI: 10.1016/0927-0256(96)00008-0

[15] Kresse G, Joubert D, From ultrasoft pseudopotentials to the projector augmented-wave method, J. Phys. Rev. B. 1999; 59: 1758. DOI: 10.1103/PhysRevB.59.1758

[16] Blochl P.E, Projector augmented-wave method, J. Phys. Rev. B. 1994; 50: 17953. DOI: 10.1103/PhysRevB.50.17953

[17] Feng J, Xiao B, Zhou R, Pan W, Clarke D.R, J. Acta Mater. 2012; 60: 3380. DOI: 10.1016/j.actamat.2012.03.004

[18] Perdew J.P, Burke K, Ernzerhof M, Phys. Rev. Lett. 1997; 78: 1396. DOI: 10.1103/PhysRevLett.77.3865

[19] Methfessel M and Paxton AT, High-precision sampling for Brillouin-zone integration in metals, Phys. Rev. B. 1989; 40: 3616-3621. DOI: 10.1103/PhysRevB.40.3616

[20] N. Papanikolaou, R. Zeller, P. H. Dederichs, N. Stefanou, Lattice distortion in Cu-based dilute alloys: A first-principles study by the KKR Green-function method, Phys. Rev. B. 1997; 55: 4157. DOI: 10.1103/PhysRevB.55.4157

[21] B.J. Inkson, H. Clemens, J. Marien, Scr. Mater., 1998 ; 38 : 1377.

[22] H. Hu, X. Wu, R. Wang, W. Li, Q. Liu, Phase stability, mechanical properties and electronic structure of TiAl alloying with W, Mo, Sc and Yb: First-principles study, J. Alloys Compd., 2016; 658: 689-696. DOI: 10.1016/j.jallcom.2015.10.270.

[23] P. Duwez and J. Taylor, Crystal Structure of TiAl, JOM., 1952; 4: 70-71. DOI: 10.1007/BF03397651.

[24] C. Zhang and H. Hu, IJMPB, 2017; 31: 1750079.

[25] P.D. Desai, Thermodynamic properties of selected binary aluminium alloy systems, J. Phys. Chem. Ref. data, 1987; 16: 109. DOI: 10.1063/1.555788.

[26] M. Blackburn, Trans Metall Soc AIME, 1967; 239: 1200.

[27] L.J. Wei, J.X. Guo, X.H. Dai, L. Guan, Y.L. Wang, B.T. Liu, Surf. Interface Anal., 2016; 48: 1337. DOI: 10.1002/sia.6043.

[28] E.A. Brandes, Smitbells Metals Reference Book (6^{th} edn). Butterworths, London.

[29] K. Tanaka and M. Koiwa, Single-crystal elastic constants of intermetallic compounds, Intermetallics, 1996; 4: S29-S39. DOI: 10.1016/0966-9795(96)00014-3.

[30] RE. Waston and M. Weinert, Transition-metal aluminide formation: Ti, V, Fe and Ni aluminides, Phys. Rev, B, 1998; 58: 5981. DOI: 10.1103/PhysRevB.58.5981.

[31] YL. Liu, LM. Liu, SQ. Wang and HQ. Ye, First-principles study of shear deformation in TiAl and Ti_3Al, Intermetallics, 2007; 15: 428-435.