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An *ab initio* study on stacking and stability of $TiAl_3$ phases

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ABSTRACT

$TiAl_3$ persists in many Al alloys and plays a detrimental role in solidification of related melts. Knowledge about $TiAl_3$ phases and phase relations is of importance to get some insight into the solidification processes, the microstructures and the properties of Al alloys. In this manuscript, we present a systematic study of the basic structures of $TiAl_3$ with aid from *ab initio* density functional theory (DFT) calculations. The study confirms that the ground state of $TiAl_3$ has the $D0_{23}$ structure, whereas the observed $D0_{22}$ type is a metastable phase. The calculations have identified the stability of a series of stacking composed of both $D0_{22}$- and $D0_{23}$-$TiAl_3$ units. At elevated temperature, the equilibrium configuration contains neither pure $D0_{23}$ nor pure $D0_{22}$ but will consist of a combination of the $TiAl_3$ cubes arranged to minimise its Gibbs energy. Stacking default investigation reveals a large energy barrier for the $D0_{22} \leftrightarrow D0_{23}$ transition. The obtained information sheds some light on the rich variety of the experimental observations in Al alloys, and further to understand the complex titanium aluminides and their thermo-structural properties.

1. Introduction

$TiAl_3$ has been a topic of intensive research due to its rich variety of phases, unique structures and industrial applications. This compound plays an important role in heterogeneous nucleation of Al alloys [1–5]. $TiAl_3$ acts as a grain refiner independently [2,3] or co-plays with TiB_2 in the widely used Al-5Ti-B or Al-3Ti-B master alloys [4]. Recently high resolution transmission electron microscopy (HRTEM) observations revealed the formation of one most-likely $TiAl_3$ atomic layer at the TiB_2 substrate in Al. This two dimensional compound (2DC) of $TiAl_3$ structure plays a crucial role in the solidification of Al alloys [5,6]. Moreover, $TiAl_3$ can be formed at Ti-Al interfaces during thermal treatments for Al alloy welding [7,8]. This indicates the importance of developing some understanding about the compound for industrial applications. Ti-Al compounds including $TiAl_3$ and their phase relations have been a subject of extensive investigations, probably just second only to the Fe-C system [9–15]. Recently, Batalu and co-workers analysed and re-evaluated the Ti-Al binary phase diagram and showed that there is no phase transition for the $TiAl_3$ (probably $D0_{22}$ structure) up to its peritectic point [9]. Schuster and Palm showed a low-temperature (LT) to a high temperature (HT) phase transition for $TiAl_3$ but without a clear transition temperature [10]. In other binary phase diagrams, a LT-HT transition occurs at 735 °C [11,12] or at about 600 °C [13–15]. There have been experimental reports on the rich variety of structures of different lengths of *c*-axis and variation of corresponding *a*-axis of the ($D0_{22}$-)$TiAl_3$ (Table 1) [7–28]. By sintering of elemental powders, Nakayama and Mabuchi obtained the cubic $L1_2$-$TiAl_3$ phase which contains some transition metal elements [7,26]. Further experiments confirmed that the $L1_2$-$TiAl_3$ phase is stabilized by impurities [27–29]. To get some insight into the relations for the $TiAl_3$ phases, theoretical methods have been employed for $TiAl_3$ [30–42]. The early first-principles simulations employed the local density functional approximation (LDA) [30–34] for the known structures and demonstrated the high stability of the $D0_{22}$-type structure [32]. Based on the available experimental values and *ab initio* calculations, Zope and Mishin built interatomic potentials for (large-scale) atomistic simulations of the Ti-Al system [36]. Using full-potential linear muffin-Tin orbital (PF-LMTO) method, Amador and co-workers investigated the influence of atomic stackings and atomic displacements from the ideal positions and revealed that the $D0_{23}$-phase is the ground state [30]. This conclusion was confirmed later by other calculations using various first-principles density-functionals [37–44] (Table 1). Zhang and Wang investigated the lattice vibration contribution to the relative stability of Ti-Al compounds, including the $TiAl_3$ phases [43]. They concluded that lattice vibration contribution doesn't change the stability order of the $TiAl_3$ phases. This is understandable since all the $TiAl_3$ phases have similar local coordination and chemical bonding. Tang and co-workers performed first-principles calculations for some one-dimensional long period structures (1D-LPSs) based on the cubic $L1_2$-$TiAl_3$ [45,46]. In the present manuscript, we have analysed systematically the existing $TiAl_3$

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Table 1
Calculated results (lattice symmetry (lat. sym.) and space group (S.G.); fractional atomic coordinates; and energy differences with respect to the formation energy of the cubic $L1_2$-$TiAl_3$ at 0 K (Eq. (1)). *n* in column one represent the number of stacking layers. The schematic structures are shown in Fig. 1.

Phase (n)	Lat. sym./S.G.	Lat. Para. (Å)	ΔE_1 (eV/$TiAl_3$)	Method and references
$L1_2$ (n = 1) Fig. 1a/1b	Cubic, Pm-3 m (No. 221)	a = 3.977	0.0	DFT-PBE this work
		a = 3.960	0.0	HSE(PBE0) this work
		Previous DFT calc.		
		a = 3.97	0.0	FP_LMTO [30]
		a = 3.908		DFT-LDA [62]
		a = 3.91		DFT-LDA [38]
		a = 3.8997		DFT-LDA [44]
		a = 3.9854		DFT-GGA [44]
		a = 3.981	0.0	DFT-GGA [40]
		a = 3.978		DFT-GGA [62]
		a = 3.9779	0.0	DFT-GGA [25]
		a = 3.9824		DFT-GGA [27]
		a = 3.977		DFT-GGA [39]
		Experimental data		
		a = 3.967		[42]
		a = 3.967–4.05		[37]]
$D0_{22}$ (n = 2) Fig. 1c	Tet.I4/mmm (No. 139)	a = 3.841, c = 8.618	−0.108	DFT-PBE this work
		a = 3.826, c = 8.571	−0.120	HSE(PBE0) this work
		Previous DFT calc.		
		a = 3.76, c = 8.50	−0.091	FP_LMTO [30]
		a = 3.847, c = 8.656		DFT-LDA [35]
		a = 3.79, c = 8.45		DFT-LDA [38]
		a = 3.7678, c = 8.4818		DFT-LDA [44]
		a = 3.8507,c = 8.6332		DFT-GGA [44]
		a = 3.847, c = 8.621		DFT-GGA [46]
		a = 3.843, c = 8.616	−0.112	DFT-GGA [40]
		a = 3.8399, c = 8.6399	−0.096	[30]
		Experimental data		[38]
		a = 3.849, c = 8.610		[19,20]
		a = 3.847*, c = 8.585		[23]
		a = 3.851, c = 8.612		[42]
		a = 3.836, c = 8.5791		[63]
		a = 3.846, c = 8.521		[64]
		a = 3.8537, c = 8.5839		[65]
		a = 3.849, c = 8.610		[67]
		a = 3.8537, c = 8.5839		[65]
N113 (n = 3) Fig. 1e	Tet.P4/mmm (No. 123)	a = 3.881, c = 12.604	−0.124	DFT-GGA, this work
$D0_{23}$ (n = 4) Fig. 1d	Tet.I4/mmm (No. 139)	a = 3.895, c = 16.662	**−0.131**	DFT-PBE this work
		a = 3.877, c = 16.595	**−0.159**	HSE(PBE0) this work
		Previous DFT calc.		
		a = 3.81, c = 16.44	**−0.101**	FP_LMTO [30]
		a = 3.8962,c = 16.6713	**−0.127**	DFT-GGA[40]
		a = 3.891, c = 16.924		DFT-GGA[42]
		Experimental data		
		a = 3.947, c = 16.679		[25,67]
		a = 3.890, c = 16.824		[42]
		a = 3.875, c = 16.916		[19]
$D0_{19}$	Hex.$P6_3$/mmm (No. 194)	a = 5.566	+0.203	
		c = 4.724		

phases and predicted various stackings by application of the one-dimensional antiphase domain (1d-APD) model [19–23,47] based on the $D0_{22}$ structure using *ab initio* density functional theory (DFT). We also performed DFT calculations with hybrid-functional correction for the three known $TiAl_3$ ($L1_2$, $D0_{22}$ and $D0_{23}$) phases. Our calculations have confirmed that the ground state $TiAl_3$ has the $D0_{23}$-type structure. The study also revealed a series of highly stable structures containing $D0_{22}$ and $D0_{23}$ components. Symmetry analysis was performed for the obtained structures of high stability. The present study suggests that many experimental observations are the 'averaged structure' of a complex series of $TiAl_3$ structures. The obtained information can serve to characterize the $TiAl_3$ structures in Al alloys, to understand other titanium aluminides in the TiAl-$TiAl_3$ partial system, and to other intermetallic systems, as well; and further to analyse the two-dimensional compounds (2DC) formed at the substrates during heterogeneous nucleation [4–6].

2. Calculational details

In this study we employed the plane wave method in the Projector Augmented-Wave (PAW) framework which has been implemented in the Vienna *Ab initio* Simulations Package (VASP) [48–51]. The exchange and correlation terms were described using the Generalized Gradient Approximation (GGA) formulations by Perdew, Burke and Ernzerhof (PBE) [52]. It has been well-established that the GGA approximation describes better the 3d transition metals (Ti in this case) and their compounds [52–54]. The cut-off energies for the wave functions and for the augmentation functions were 550 eV and 700 eV, respectively. These values are higher than the default values, 178.330 eV and 328.883 eV for Ti; and 240.300 eV and 291.052 eV for Al. This serves to get high accurate valence-electrons' energies. The electronic wave functions were sampled on very dense grids, in the irreducible Brillouin zone (BZ) for the crystals, e.g. 20 × 20 × 20 grid (220 *k*-points) for the cubic $L1_2$-$TiAl_3$ unit cell, using the Monkhorst and Pack