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Prediction of the ordering behaviours of the orthorhombic phase based on Ti_2AlNb alloys by combining thermodynamic model with *ab initio* calculation

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Abstract

The order–disorder transformation of intermetallics is of fundamental and technical importance. The ordering behaviours of the O phase based on Ti_2AlNb alloys are predicted by combining thermodynamic model with *ab initio* calculation. The site occupying tendencies of the constituent elements are studied for the first time theoretically without referring experimental data as input. The predicted results show that Al atoms always tend to occupy the γ (4*c*1) sublattice, Ti atoms tend to occupy the α (8*g*) sublattice and Nb atoms the β (4*c*2) sublattice. The ordering tendencies of Ti and Nb atoms decrease with the increase of temperature, while the site occupation of Al atoms is weakly dependent on the temperature. The order–disorder transformation belongs to a second-order transition with a continuous character. It is also predicted that for the nonstoichiometric O phase with Al contents higher than 25 at.%, the site occupancies of the excess Al atoms prefer the β sublattice. The predicted site occupancy fractions and order parameters agree well with the reliable experimental data. The prediction has been improved compared with the Gorsky–Bragg–Williams model, as well as our early LMTO-ASA calculations.

Keywords: A. Ternary alloy systems; B. Order/disorder transformations; D. Site occupancy; E. *Ab initio* calculations; E. Phase stability, prediction

1. Introduction

Ti_2AlNb-based alloys are of great technological interest in high temperature applications since they have a higher strength-to-density ratio and better room temperature ductility and fracture toughness than conventional titanium aluminides, with no sacrifice in elevated temperature properties. They have attracted considerable attention during the past two decades [1–4] since Banerjee et al. [5,6] from India identified an ordered orthorhombic phase in Ti_3Al–Nb system and designated it as the O phase in 1988. Ti_2AlNb-based alloys may consist of O, B2 and/or α_2 phases depending on the alloy composition and heat treatment condition [1,2,4]. And the O phase is the dominating phase, so its order–disorder transformation is of fundamental and technical importance [7]. So far, the investigations concerning the order–disorder transformation of the O phase are very limited. Mozer et al. [8] studied the site occupations of O phase based on the Ti_2AlNb stoichiometry by neutron diffraction (ND). Muraleedharan et al. [9] studied the site occupations of alloying elements in the orthorhombic phase with composition as Ti–27.5Al–*z*Nb (where $z = 25$, 20 or 17.5) by atom location channelling enhanced microanalysis (ALCHEMI) and simulated the order–disorder transformation

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of the O phase with aluminum content fixed at 25 at.% by using a Gorsky–Bragg–Williams (G–B–W) model. Several years later, new experimental data were reported from the same laboratory in India [11]. These two sets of data do not agree with each other and no full disorder phase was reported in the new experiment at 1173 K. Wu et al. [10] and Singh et al. [11] predicted the order–disorder transformation and recurred the "weak" first-order transition character in an extended composition range with G–B–W model. Sarosi et al. [12] studied the order behaviours for Ti–23Al–20Nb and Ti–27.5Al–23Nb orthorhombic alloy by ALCHEMI and ND methods and characterized them with a series of ordering tie triangles. The crystallographic information [5,8,13] of the completely ordered O phase based on stoichiometric Ti_2AlNb is given in Table 1. For the convenience of statement, generally, in Ti_2AlNb-based O phase, α denotes the 8*g* sublattice, β denotes the 4*c*2 sublattice and γ denotes the 4*c*1 sublattice. Of the total number of sites, 50% belongs to the α sublattice, 25% belongs to the β sublattice, and the rest belongs to the γ sublattice. The available experimental results of site occupancy fractions and order parameters are summarized in Table 2. From Table 2, it is seen that it is not easy to measure the site occupancy fractions, especially in the case of nonstoichiometric O phase. In this paper, the experimental data available at 973 K from Mozer et al. [8] by ND technique for the stoichiometric compound Ti_2AlNb (Ti–25Al–25Nb) are accepted as reliable experimental results. And considering the big difference of the experimental data for some compositions in Refs. [9,11], for the nonstoichiometric alloy, the experimental data of Ti–27.5Al–25Nb from Ref. [11] at 973 K as well as the experimental data of Ti–27.5Al–20Nb from Ref. [9] at 1173 K are not accepted. Furthermore, when the G–B–W model is employed to predict the order–disorder transformation of O phase based on Ti_2AlNb alloys, the inherent limitations very often hamper us to get a reliable result. Firstly, one has to refer the experimental results in the G–B–W model, while it is not easy to obtain the reliable experimental data in most case as mentioned above. Secondly, only the first nearest neighbor interactions are taken into account in the G–B–W model. In fact, the distance between the second nearest neighbors is just about two times of the distance between the first nearest neighbors (the distance between the first nearest neighbors is 2.9 ± 0.15 Å and the distance between the second nearest neighbors is 4.8 ± 0.5 Å), so one can image that the error of the interaction energy is unacceptable in the real many-body system. Servant and Ansara [14] described the ordering behaviours of the O phase with thermodynamic models, and the experimental results from Muraleedharan et al. [9] were adopted. Due to the complication of the phase relationship in the Ti–Al–Nb ternary system and a large number of thermodynamics' parameters to optimize, the exact site occupancy fractions of the alloying elements were still unavailable.

With the availability of powerful computers, reliable models, and efficient algorithms, nowadays, the combination of *ab initio* electronic structure calculation and computational thermodynamics has attracted more and more attention [15–17]. In our early work [18,19], the order behaviours of the O phase based on Ti_2AlNb alloys were studied by combining the general three-sublattice model with *ab initio* calculation [16,17], where the method formulated within the linear muffin-tin-orbital method in the atomic-sphere approximation (LMTO-ASA) [20] was employed to execute the *ab initio* total energy calculations. However, the LMTO-ASA method does not seem very convenient in systems presenting large size mismatch and in structures which are not closely packed, the predicted results are not satisfied although it has been improved compared with the G–B–W model. The most accurate and therefore the most computationally intensive techniques are the full-potential methods [15], nevertheless, the projector augmented wave (PAW) potential method [21,22] is the state-of-the-art in electronic calculations because it is almost as fast as the usual ultrasoft pseudopotential (US-PP) method [23,24] and gives energies very close to the best full-potential linearized augmented-plane-wave (FLAPW) calculations [25]. To conclude the currently used methods, the Vienna *ab initio* simulation package (VASP) [26–28] can be used with success in metallic system. VASP is based on the density functional theory (DFT) [29] within the local density approximations (LDAs) [30] or the generalized gradient approximations (GGAs) [31–33]. It is a plane-wave code. In the present paper, the ordering behaviours of the O phase based on Ti_2AlNb alloy are revisited and VASP is employed to fulfill the *ab initio* total energy calculation. The paper is presented in five sections. In Section 2, the general three-sublattice model is described. In Section 3, the details of the *ab initio* calculation on the stable pure elements and the end-member compounds are presented. In Section 4, the site occupancy fractions are calculated and the ordering behaviours are analyzed. The conclusions are presented in Section 5.

Table 1
The crystallographic information of the completely ordered O phase based on Ti_2AlNb stoichiometry [5,8,13]

Element	Multiplicity, Wyckoff notation	Point symmetry	Internal parameter of atomic coordinates		
			x	*y*	*z*
Ti	α (8*g*)	*m*	0.2310	0.9041	0.25
Al	γ (4*c*1)	*m*2*m*	0	0.1633	0.25
Nb	β (4*c*2)	*m*2*m*	0	0.6357	0.25

Orthorhombic, space group: *Cmcm*, no. 63; prototype: NaHg; Pearson symbol: oC16; lattice parameters: $a = 6.09$ Å, $b = 9.57$ Å, $c = 4.67$ Å, $\alpha = \beta = \gamma = 90°$, $V = 271.93$ Å^3.

2. Sublattice model

The thermodynamics properties of the O phase based on Ti_2AlNb can be considered by the following general three-sublattice model according to the crystallographic information

$$\left(Ti_{y_{Ti}^{\alpha}} Al_{y_{Al}^{\alpha}} Nb_{y_{Nb}^{\alpha}}\right)_{0.5} \left(Ti_{y_{Ti}^{\gamma}} Al_{y_{Al}^{\gamma}} Nb_{y_{Nb}^{\gamma}}\right)_{0.25} \left(Ti_{y_{Ti}^{\beta}} Al_{y_{Al}^{\beta}} Nb_{y_{Nb}^{\beta}}\right)_{0.25} \quad (1)$$