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Site occupations and ordering behaviour of *O* phase in Ti₂AlNb-based intermetallics^①

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[Abstract] The site occupations of the alloying elements of *O* phase in Ti₂AlNb-based intermetallics are clarified. The ordering behaviours of the *O* phase in Ti₂Al_{1-y}ZNb (y ≥ 25%, mole fraction) orthorhombic alloys are also investigated with a Bragg-Williams model. In the temperature range where the *O* phases exist, the order parameters change with the alloy composition and temperature continuously, and the first-order transition character is very "weak".

[Key words] Ti₂AlNb-based intermetallics; orthorhombic phase; site occupation; ordering behaviour

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1 INTRODUCTION

The orthorhombic alloys are of great technological interest in high temperature applications since they have a good balance among strength-to-density ratio, ductility, fracture toughness and creep resistivity. The new alloy family based on Ti₂AlNb has received considerable attention^[1-5] during the past decade since Banerjee et al^[6] identified the orthorhombic *O* phase in 1988. The *O* phase is a complex ternary ordering intermetallic phase and there exists an order-disorder transition between *O*₂ and *O*₁ phase^[7]. As we know, long-range ordering behaviour in alloy will increase the elastic modulus and flow stress, and decrease the mobility of the atoms and creep rate^[8], so it is essential to understand the ordering behaviour of the *O* phase. However, the literature concerning the order-disorder transition of the *O* phase is rare except a paper published by Muraleedharan et al^[7] in *Journal of Intermetallics* in 1995. We noted some obvious mathematical deficiency by examining the deducing procedure:

1) The original equation " $P_{\beta}^{\text{Nb}} = 1.33C - 0.33s$ (B6)" should be " $P_{\alpha}^{\text{Nb}} = 1.33C - 0.33s$ (B6)";

2) The original equation " $\omega = N \sum_i x_i \ln x_i$ (B11)" should be " $\ln \omega = N \sum_i x_i \ln x_i$ (B11)";

3) The original equation " $\left[\frac{\partial(T\Delta S)}{\partial s} \right]_{T,C} = 0.167$
• $KTN \ln Z$, where $Z = \frac{(1-1.33C+0.33s)^2}{(1-1.33C+0.67s)^4}$.

$\frac{(1.33C+0.67s)^4}{(1.33C-0.33s)^2}$ " contains some mathematical mistakes. The correct form should be " $\left[\frac{\partial(T\Delta S)}{\partial s} \right]_{T,C} =$

$-0.167 KTN \ln Z$, where $Z = \frac{(1-1.33C+0.33s)^2(1.33C+0.67s)^4}{(1-1.33C-0.67s)^4(1.33C-0.33s)^2}$.

In this paper, the site occupations of the alloying elements and order-disorder transition of Ti₂Al_{1-y}ZNb (y ≥ 25) (mole fraction, %) orthorhombic alloys are investigated. The relationship among the long-range order parameter (*s*), temperature (*T*), and the composition of the orthorhombic phase (*y*, *z*) is established so as to obtain a rational result.

2 SITE OCCUPATION AND THE ORDERING BEHAVIOR OF *O* PHASE

2.1 Site occupation of alloying element

Banerjee et al^[6,7] identified the *O* phase is an orthorhombic phase with Cmc₂m symmetry. We consider the three sublattices for *O* phase as α (8g), β (4c2) and γ (4c1) (the multiplicity Wyckoff notations are given in the brackets). Of the total number of sites, 50% belongs to the α sublattices, 25% belongs to the β sublattices, and the rest 25% belongs to γ sublattices. Mozer et al^[9] studied the site occupations of the *O* phase based on the Ti₂AlNb stoichiometry by neutron diffractometry (ND) and the results showed that Al atoms occupy all the γ sites. In completely ordered *O*₂ phase with Ti₂AlNb stoichiometry, the α sites contain only Ti atoms, the β

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sites contain only Nb atoms and the γ sites contain only Al atoms. Fig. 1 shows the projection of the completely ordered and completely disordered orthorhombic lattices in [001] direction respectively. And the structure report of the completely order $O2$ phase is showed in Table 1.

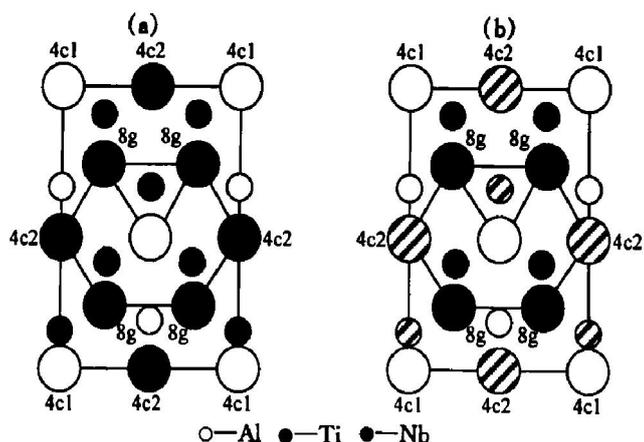


Fig. 1 Projection of orthorhombic lattice with Ti_2AlNb stoichiometry in [001] direction
 (a) —Completely disordered $O1$ phase;
 (b) —Completely ordered $O2$ phase

Table 1 Structure report of completely ordered $O2$ phase with Ti_2AlNb stoichiometry
 (Orthorhombic, $Cmcm$, $a = 6.09 \text{ \AA}$ $b = 9.57 \text{ \AA}$ $c = 4.67 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$)

Atom	Wyckoff notation	Point symmetry	Coordinates of equivalent position		
			x	y	z
Ti	$\alpha(8g)$	m	0.231	-0.0959	0.25
			-0.231	-0.0959	0.25
			-0.231	0.0959	0.75
			0.231	0.0959	0.75
			0.731	0.4041	0.25
			0.269	0.4041	0.25
			0.731	0.5959	0.75
			0.269	0.5959	0.75
Al	$\gamma(4c1)$	mm	0	0.1633	0.25
			0	-0.1633	0.75
			0.5	0.6633	0.25
			0.5	0.3367	0.75
Nb	$\beta(4c2)$	mm	0	-0.3643	0.25
			0	0.3643	0.75
			0.5	0.1357	0.25
			0.5	0.8643	0.75

For the nonstoichiometric O phase with Al content higher than 25%, Al atoms not only occupy all the γ sites, but also occupy some of the α and β sites. From the atom location channeling enhanced microanalysis (ALCHEMI) results of $Ti_{27.5}Al_{z}Nb$ ($z = 17.5 \sim 25$) orthorhombic alloys by Muraleedharan et al^[7], the Al atoms which are in excess of stoichiometry will occupy some of the α and β sites with equal probability. For the nonstoichiometric $O2$ phase which Al content is less than 25%, some of the Ti and Nb atoms will occupy the rest γ sites, but the detail is very complicated. In completely disordered $O1$ phase, the Al atoms occupy their sites regularly, while the Ti and Nb atoms will occupy the α , β and the rest γ sites randomly. For the convenience of un-

derstanding, we only investigated the ordering behaviors of the $Ti_{27.5}Al_{z}Nb$ ($\gamma \geq 25$) orthorhombic alloy and did not consider the case of $\gamma < 25$ in the present study.

2.2 Ordering behaviour of orthorhombic phase

Considering the site occupations of the alloying elements, we have

$$P_{\alpha}^{Ti} + P_{\alpha}^{Nb} + P_{\alpha}^{Al} = 1, P_{\beta}^{Ti} + P_{\beta}^{Nb} + P_{\beta}^{Al} = 1 \quad (1)$$

where $P_{\alpha, \beta}^{Ti, Nb, Al}$ is the probability of finding Ti, Nb or Al atoms at the α or β sites. Because Al atoms occupy their sites regularly, we have

$$P_{\alpha}^{Al} = P_{\beta}^{Al} \quad (2)$$

From Eqns. (1) and (2), we get

$$P_{\alpha}^{Ti} - P_{\beta}^{Ti} = P_{\beta}^{Nb} - P_{\alpha}^{Nb} \quad (3)$$

So we define an order parameter, s , as

$$s = P_{\alpha}^{Ti} - P_{\beta}^{Ti} = P_{\beta}^{Nb} - P_{\alpha}^{Nb} \quad (4)$$

Since Bragg and Williams first produced a rigorous theory of order-disorder transitions, the theory has been improved. The Bragg-Williams theory is based on the model which involves the following assumptions: 1) the atoms are at rest on the lattice sites; 2) only the first nearest neighbor interactions are taken into account.

For convenience of analysis, we suppose the total number of atoms is 100, so the numbers of the α sites, β sites and γ sites are 50, 25 and 25, respectively.

According to the ALCHEMI results^[7], the Al atoms in excess of the stoichiometry will occupy the α and β sites with equal probability, therefore we have

$$P_{\alpha}^{Al} = P_{\beta}^{Al} = (\gamma - 25) / 75 \quad (5)$$

The mass balance equation of Ti atoms is

$$50P_{\alpha}^{Ti} + 25P_{\beta}^{Ti} = 100 - \gamma - z \quad (6)$$

Similarly for Nb atoms:

$$50P_{\alpha}^{Nb} + 25P_{\beta}^{Nb} = z \quad (7)$$

From Eqns. (4), (6) and (5), we get

$$P_{\alpha}^{Ti} = (100 - \gamma - z + 25s) / 75 \quad (8)$$

$$P_{\beta}^{Ti} = (100 - \gamma - z - 50s) / 75 \quad (9)$$

$$P_{\alpha}^{Nb} = (z - 25s) / 75 \quad (10)$$

$$P_{\beta}^{Nb} = (z + 50s) / 75 \quad (11)$$

For a certain temperature and composition, we now consider the stability of the thermodynamics when O phase order from the completely disordered $O1$ phase ($s = 0$) to a certain ordering state. The change of total Gibbs energy is

$$\Delta G = \Delta H - T \Delta S \quad (12)$$

When the order-disorder transition reach its phase equilibrium, the total Gibbs energy change must present an extremum, so

$$\left[\frac{\partial(\Delta G)}{\partial s} \right]_{T, y, z} = \left[\frac{\partial(\Delta H)}{\partial s} \right]_{T, y, z} - \left[\frac{\partial(T \Delta S)}{\partial s} \right]_{T, y, z} = 0 \quad (13)$$

So when the ΔH and ΔS are described with s , T , y and z , we can get a relationship among the s , T , y and z according to Eqn. (13).

ΔH corresponds to the interatomic bonds. From the structure report of the completely ordered $O2$ phase, we know that each α site has 4α , 4β and 4γ first nearest neighbours. Similarly β site has 8α and 4γ first nearest neighbours, and γ site has 8α and 4β first nearest neighbours. So we can get that the total number of $Ti-Nb$ bonds among the first nearest neighbour sites is

$$N_{Ti-Nb} = 200(P_{\alpha}^{Ti}P_{\alpha}^{Nb} + P_{\alpha}^{Ti}P_{\beta}^{Nb} + P_{\alpha}^{Nb}P_{\beta}^{Ti}) \quad (14)$$

Similarly the total number of $Ti-Al$ bonds among the first nearest neighbour sites is

$$N_{Ti-Al} = 200(P_{\alpha}^{Ti}P_{\alpha}^{Al} + P_{\alpha}^{Ti}P_{\beta}^{Al} + P_{\alpha}^{Al}P_{\beta}^{Ti} + P_{\alpha}^{Ti}) + 100P_{\beta}^{Ti} \quad (15)$$

And the total number of $Nb-Al$ bonds among the first nearest neighbour sites is

$$N_{Nb-Al} = 200(P_{\alpha}^{Nb}P_{\alpha}^{Al} + P_{\alpha}^{Nb}P_{\beta}^{Al} + P_{\alpha}^{Al}P_{\beta}^{Nb} + P_{\alpha}^{Nb}) + 100P_{\beta}^{Nb} \quad (16)$$

When O phase order from the completely disordered $O1$ phase ($s=0$) to a certain ordering state, the change of the number of $Ti-Nb$, $Ti-Al$ and $Nb-Al$ bonds is

$$\Delta N = N|_s - N|_{s=0} \quad (17)$$

So we get that

$$\begin{aligned} \Delta N_{Ti-Nb} &= 66.67s^2, \quad \Delta N_{Ti-Al} = 0, \\ \Delta N_{Nb-Al} &= 0 \end{aligned} \quad (18)$$

The change of the total interatomic bonds is

$$\begin{aligned} \Delta H &= \Delta N_{Ti-Nb}(-V_{Ti-Nb}) + \Delta N_{Ti-Al} \cdot \\ &\quad (-V_{Ti-Al}) + \Delta N_{Nb-Al}(-V_{Nb-Al}) \\ &= \Delta N_{Ti-Nb} \cdot (-V_{Ti-Nb}) \end{aligned} \quad (19)$$

$$V = H_{A-B} - \frac{H_{A-A} + H_{B-B}}{2} \quad (20)$$

where V is the $A-B$ interchange energy, and H_{A-B} , H_{A-A} and H_{B-B} are the energies of $A-B$, $A-A$ and $B-B$ bonds, respectively. According to Faraks et al^[10] by embedded atom method (EAM), the values of H_{Ti-Nb} , H_{Ti-Ti} and H_{Nb-Nb} are 6.215 eV/atom, 4.850 eV/atom and 7.470 eV/atom, respectively. So we get, $V_{Ti-Nb} = 0.055$ eV/atom.

$$\left[\frac{\partial(\Delta H)}{\partial s} \right]_{T, y, z} = -133.34s \cdot V_{Ti-Nb} \quad (21)$$

On the other hand, the change of configuration entropy in the system is

$$\Delta S = S|_s - S|_{s=0} \quad (22)$$

$$S = -K \sum_i N_i \cdot P_i^j \cdot \ln P_i^j \quad (23)$$

So we get

$$\left[\frac{\partial(T\Delta S)}{\partial s} \right]_{T, y, z} = -16.667K \left[\ln \frac{(100-y-z+25s)(z+50s)}{(100-y-z-50s)(z-25s)} \right] \quad (24)$$

From Eqn. (13), we obtain a relationship among

the long-range order parameter (s), temperature (T), and the composition of the orthorhombic phase (y, z)

$$T = \frac{8sV_{Ti-Nb}}{\left[K \ln \frac{(100-y-z+25s)(z+50s)}{(100-y-z-50s)(z-25s)} \right]} \quad (25)$$

Since the Boltzmann constant K is 8.6194×10^{-5} eV/(atom \cdot K), we have $V/K = 638.1$ K. Therefore

$$T = \frac{5104.8s}{\ln \left[\frac{(100-y-z+25s)(z+50s)}{(100-y-z-50s)(z-25s)} \right]} \quad (26)$$

Hence, when the compositions of the orthorhombic alloy are given, we obtain the value of the order parameter s at different temperature T by solving Eqn. (26) numerically.

2.3 Results and discussion

Fig. 2 is Bragg-Williams plot of the order parameter of the $O2$ phase based on $Ti-25Al-25Nb$. The experimental data from Mozer et al by ND is superimposed. Fig. 3 is Bragg-Williams plot of the order parameter of the $O2$ phase based on $Ti-27.5Al-25Nb$. The experimental data from Muraleedharan et al by ALCHEMI are superimposed and can be seen to be very dispersive. Fig. 4 is Bragg-Williams plot of the order parameter of the $O2$ phase based on $Ti-25Al-zNb$.

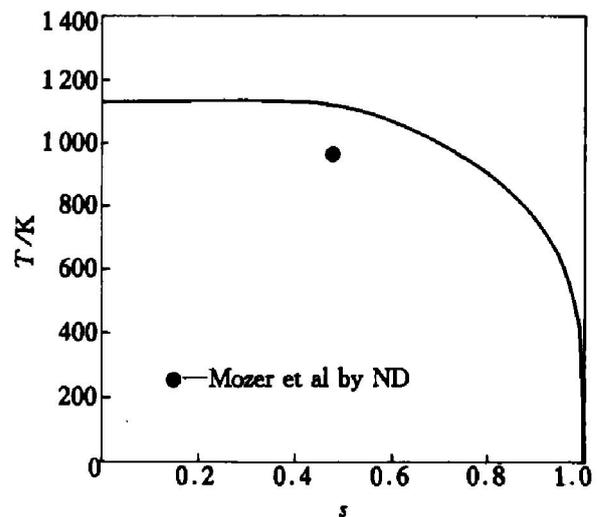


Fig. 2 Bragg-Williams plot of order parameter of $O2$ phase based on $Ti-25Al-25Nb$ with experimental data superimposed

The above plots show that in the temperature range where the O phases exists, the order parameters change with the alloy composition and temperature continuously, and the first-order transition character is very "weak" on the curve of order parameter (s) vs temperature (T) of which the order parameter changes with the temperature abruptly at T_c (order \leftrightarrow disorder transition temperature). The comparison of the order parameters from present theoretical prediction and available experimental data illustrates the

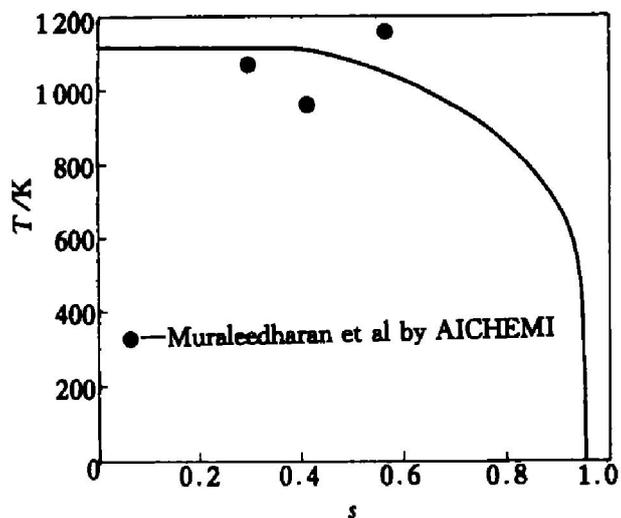


Fig. 3 Bragg-Williams plot of order parameter of *O*2 phase based on Ti-27.5Al-25Nb with experimental data superimposed

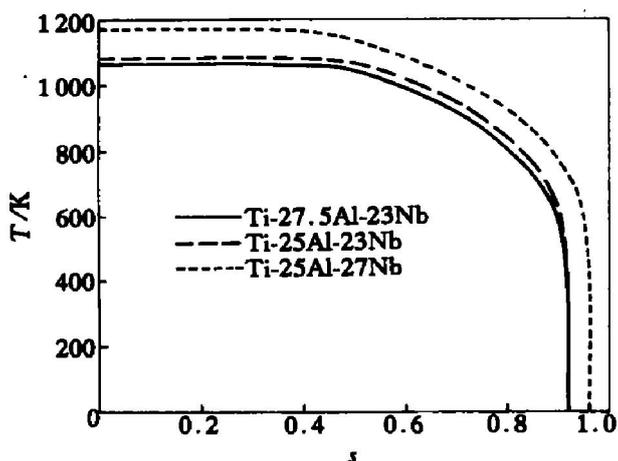


Fig. 4 Bragg-Williams plot of order parameter of *O*2 phase based on Ti-25Al-zNb

kinetic difficulty in attaining its equilibrium order in the *O* phase at lower temperatures.

3 CONCLUSION

In the temperature range where the *O* phase exists, the order parameters change with the alloy com-

position and temperature continuously, and the first-order transition character is very "weak".

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