EFFECTS OF INTERSTITIAL IMPURITIES ON PHASE TRANSFORMATION OF Ti-Al ALLOYS①

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ABSTRACT According to the Average Lattice and Atom Models of the Empirical Electron Theory of Solids and Molecules(EET), effects of interstitial impurities on valence electron structures and phase transformation of Ti-Al alloys are analyzed, and descendant degree of bond energy, melting point and liquidus temperatures affected by interstitial impurities are calculated by the bond energy formula of the EET, and then the main experimental results which are not confirmed about phase transformation in Ti-Al alloys are explained. The results are that, because of the effects of interstitial impurities, atom states increase, bond structures are seriously anisotropic, $\beta \rightarrow \alpha$ transformation is hindered, and the phase transformation in an intermediate content is very complex. Also, the melting point and liquidus temperatures decrease, and average decreased degree is estimated through approximation by the EET.

Key words Ti-Al alloys phase transformation valence electron structure interstitial impurities

1 INTRODUCTION

The titanium-aluminide compounds have received considerable attention recently as candidate materials for relatively high temperature uses such as turbine engine components. The major disadvantages of these materials are their low ductilities and toughnesses at room temperature. Considerable improvements in these properties have been achieved by alloying and thermal-mechanical processing[1,2]. However, the success of these methods has been hindered by the lack of a thorough understanding of phase thransformation or/and phase diagram for alloys in this system. In particular, the relationships between the intermediate phases have been the subject of considerable debate[3-6]. Besides experimental ways and test techniques, the intense action between different interstitial impurities (IIs) O, N, C, H and Ti, Al atoms is a main factor which affects accurate testing of Ti-Al diagram in experiment. A small amount of IIs can have a drastic effect on the position of the phase boundaries of an equilibrium diagram or the stability of a phase. It is the important effect of IIs that results in doubtful or uncertain phase transformation in Ti-Al alloys. Surprisingly however, various studies on the phase transformation in Ti-Al alloys hardly involved the important effect, and quantitative analysis was not reported. The main reason is that the phase transformation question can be explained by electron theory, but it is very abstruse and complicated to deal with the important effect in physics and maths because of involving complex action between electron, crystal lattice and interstitial atoms.

The Empirical Electron Theory of Solids and Molecules (EET)[7] affords a concise and practical Bond Length Difference (BLD) method to calculate the electron structure. According to the method and the Average Crystal Lattice and Atom Model of EET, the effects of IIs on

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valence electron structure (VES) were analyzed so that a new way could be ushered to reckon quantitatively or semiquantitatively effective degree of IIs on the phase transformation in Ti-Al alloys, and the direct data were applied to explain doubtful experimental results.

2 EFFECT OF IIs ON VESs

2.1 VESs of various phases in Ti-Al alloys

VESs of α-Ti, β-Ti, Ti_3Al (α_2), TiAl (γ), $TiAl_3$ and pure Al phases in Ti-Al alloys were calculated by computer according to the BLD method of EET. The calculated results[8] are listed in Table 1.

Table 1 Bond structures of phases in Ti-Al system

Material	Constants	Bond	I_α	n_α
β-Ti	a = 0.3313 nm, σ_{Ti} = Al0	A	8	0.2806
		B	6	0.0513
α-Ti	a = 0.2950 nm, c = 0.4688 nm, σ_{Ti} = Al0	A	6	0.2472
		B	6	0.2070
		C	6	0.0045
Ti_3Al	a = 0.5782 nm, c = 0.4629 nm, σ_{Ti} = Al3, σ_{Al} = A4	A	12	0.2560
		B	12	0.2440
		C	12	0.2296
		D	12	0.2198
TiAl	a = 0.4005 nm, c = 0.4070 nm, σ_{Ti} = Al4, σ_{Al} = A4	A	4	0.2559
		B	4	0.2375
		C	16	0.2283
		D	4	0.0053
$TiAl_3$	a = 0.3843 nm, c = 0.8596 nm, σ_{Ti} = Al4, σ_{Al} = A4	A	8	0.3316
		B	8	0.3177
		C	16	0.1676
		D	16	0.1750
Al	a = 0.4049 nm, σ_{Al} = A4	A	12	0.2086
		B	6	0.0045

a, c —Lattice constants; σ—Hybridization state; I_α—Bond numbers; n_α—Covalent electron numbers

2.2 VESs of various phases with IIs

VESs of solid solution phases with O, N, C and H can be calculated according to the Average Crystal Lattice Model of EET, i.e. interstitial solid solution may be thought as an ideal mixture of crystal lattices with and without interstitial atoms. The VESs of various phases without interstital atoms above were calculated as before. The crystal lattice with IIs is analyzed as follows.

(1) Position of IIs

O, N, C and H can be in the largest interstitial positions of every crystal lattice. The crystal structure of α-Ti is A3, and its most interstitial position is octahedron; and β-Ti, A2, tetrahedron; and γ, $L1_0$, approximate tetrahedron; and α_2, DO_{19}, approximate octahedron, and $TiAl_3$, DO_{22}, approximate tetrahedron too.

(2) Solubility of IIs

Ti-Al alloys are susceptible to IIs, but it is known from Refs.[9, 10] that the real solubility of Ti-Al alloys is not more than 2.0% (mole fraction), thus the crystal lattice with IIs can contain at most only one interstitial atom.

(3) Lattice constant of crystal lattice with IIs

Because the solubility of IIs is small, which results in small distortion of crystal lattice, the lattice constant of crystal lattice with IIs is approximately equivalent to that without IIs.

The VES of crystal lattice with O, N, C or H atom has been calculated according to the Average Crystal Lattice Model. The results are that effects of IIs on the bond structure of solid phase are similar because of low and approximate solubility, small atom radium and maximum interstice location of IIs, i.e. IIs make hybridization states of atoms and covalent electron numbers increase, and lattice electron numbers and binding energy of system decrease. To concisely and quantitatively reckon the comprehensive effect of common IIs on VES, we approximately think of O, N, C and H as a kind of equivalent "average interstitial atom" to simplify calculation, i.e. numbers of covalent and lattice electron and single bond radii are given by these equations:

$$n_c = an_c^O + bn_c^N + cn_c^C + dn_c^H$$

$$n_l = an_l^O + bn_l^N + cn_l^C + dn_l^H$$

$$R_{(1)} = aR_{(1)}^O + bR_{(1)}^N + cR_{(1)}^C + dR_{(1)}^H$$

where a, b, c and d are proportion coefficients of real solubility of IIs which are obtained from Refs.[9, 10]. The VESs of crystal lattice with IIs were calculated by the BLD method. The results are listed in Table 2 where A bond is the strongest bond, and A′, B′ and C′ bonds are the corresponding A, B and C bonds of crystal lattice without IIs, respectively.

2.3 Discussion

As indicated in Table 2, IIs result in a rise of hybridization states of Ti and Al atoms, and change VESs of crystal lattice with IIs. Generally, the strongest bond of crystal lattice with IIs is formed between IIs and metal atoms where numbers of covalent electron are much more than that without IIs while A′, B′ and C′ bonds formed between Ti and Al atom are weakened by IIs, and their numbers of covalent electrons are decreased. At the same time, numbers of lattice electrons of crystal lattice with IIs are also decreased very much. From the above we conclude that IIs make the bonds stronger in some directions and weaker in others, which results in seriously anisotropic bond structure. Because of the different crystals and bond structures of the different phases, the difference of the effect of IIs is very large. Generally, original A and B bonds of α-Ti and β-Ti are weakened seriously firstly, and those of Ti_3Al and TiAl secondly, and those of $TiAl_3$ thirdly. Even if comparing α-Ti with β-Ti of solid solution as well as Ti_3Al with TiAl of ordered compound, there is a little difference in effect of IIs on bond structures. It is the difference as well as the comprehensive effect of content and temperature that results in very seriously anisotropic bond structure of these alloy phases, which promotes or hinders some phase transformations too. This is the natural reason why IIs affect phase transformation in Ti-Al alloys. Thorough analysis depends on concrete phases and the external conditions as follows.

Table 2 VESs of Ti-Al alloys with average IIs

Material	Constants	Bond	I_α	n_α
α-Ti	σ_{Ti} = Al 3, σ_{Al} = 4, σ_O = 2, σ_N = 1, σ_C = 6, σ_H = A4	A	12	0.9186
		A′	18	0.1586
		B′	18	0.0943
β-Ti	σ^{I}_{Ti} = Al 3, σ^{II}_{Ti} = Al 4, σ_{Al} = 4, σ_O = 2, σ_N = 1, σ_C = 6, σ_H = A4	A	4	0.8761
		A′	16	0.1941
		B′	16	0.0431
TiAl	σ^{I}_{Ti} = Al 6, σ^{II}_{Ti} = Al 7, σ_{Al} = 5, σ_O = 2, σ_N = 1, σ_C = 6, σ_H = A4	A	8	0.9761
		A′	8	0.1461
		B′	8	0.1374
		C′	16	0.1258
Ti_3Al	σ_{Ti} = Al 6, σ_{Al} = 5, σ_O = 2, σ_N = 1, σ_C = 6, σ_H = A4	A	12	0.9236
		A′	12	0.1470
		B′	12	0.1230
		C′	12	0.1211
$TiAl_3$	σ_{Ti} = Al 7, σ_{Al} = 5, σ_O = 2, σ_N = 1, σ_C = 6, σ_H = A4	A	8	1.2305
		A′	16	0.2894
		B′	16	0.2819
		C′	32	0.1568

3 EFFECTS OF IIs ON PHASE TRANSFORMATIONS IN INTERMEDIATE Ti-Al ALLOYS

3.1 Effecs of IIs on invariant reaction

It is indicated that to compare main A′ and B′ bonds of α-Ti with that of β-Ti with IIs, the degree of the effect of IIs on their bond structures must be different. The main bond energies of α-Ti and β-Ti listed in Table 3 can be calculated by bond energy formula of the EET. As indicated in Table 3, bond energy of α-Ti decreases more greatly than that of β-Ti does, which makes system stability lower and hinders allotropic transformation $\alpha \rightarrow \beta$. It is also thought that IIs make VES of β-Ti more stable than that of α-Ti at $\beta \rightarrow \alpha$ transformation temperature. So, reconstruction transformation in which crystal structure of β-Ti is broken to form that of α-Ti is restrained, i.e. IIs play a role in stablilizing β-Ti and hindering $\beta \rightarrow \alpha$ transformation. At present, it is the same as the mechanism for hydrogen as a temporary element to form β phase microstructure at room temperature and increase toughness of Ti-aluminides. Analyzing the phase transformation in intermediate Ti-Al alloys by the mechanism, we can learn that two peritectics $L + \beta \rightarrow \alpha$, and $L + \alpha \rightarrow \gamma$ should occur at high temperatures as McCullough *et al* thought, but the two peritectics do not actually occur because of the locking effect of IIs on β phase which results in stable β phase, and kinetic reason. Ordered γ phase $L1_0$ crystal structure similar to that of β phase can be produced finally as the temperature decreases, which is the thermodynamic reason why there is only one peritectics $L + \beta \rightarrow \gamma$ in Murray's Ti-Al phase diagrams. Similarly, doubtful experimental results on α_2/α phase boundary and invariant reaction $\alpha_2 + \gamma \rightarrow \alpha$

Table 3 Descendant degree of bond energy affected by IIs

E	Bond energy	Bond energy with IIs	Descendant degree
E_α/(kJ·mol^{-1})	24.176	21.894	9.44 %
E_β/(kJ·mol^{-1})	28.435	26.213	7.81 %

can be explained according to these analyses.

3.2 Effect of IIs on metastable phases

The crystal structure of metastable phase Ti_2Al is similar to that of α_2, which is an intermediate phase during transformation of α_2 to γ, i.e. transformation of $\alpha_2 \rightarrow Ti_2Al \rightarrow \gamma$ arises and obeys the crystal orientation relations as follows[5]:

$$[011]_\gamma \parallel [11\bar{2}0]_{Ti_2Al} \parallel [11\bar{2}0]\alpha_2$$

$$(11\bar{1})_\gamma \parallel (0001)_{Ti_2Al} \parallel (0001)\alpha_2$$

So, the transformation of α_2 to Ti_2Al is a typical one of displacement, and Ti_2Al to γ is one of reconstruction. If the kinetic condition is met, there will be a Ti_2Al phase during the complete transformation of α_2 to γ. However, as shown in Table 2, the main bond A', B' and C' of α_2 phase are weakened more seriously than that of γ phase by the effect of IIs, thus stability of α_2 will be lower than that of γ. So, reconstruction transformation of α_2 or Ti_2Al to γ phase is hindered relatively because of effect of IIs. At the same time, displacement transformation of α_2 to Ti_2Al does not need breaking main bonds, i.e. the locking effect of IIs is very weak, and the transformation can arise easily. Therefore metastable phase Ti_2Al is easy to form and even exists at room temperature because of the incomplete transformation of α_2 to γ phase by the effect of IIs as kinetic condition is favourable like quick cooling. The transformation of metastable phase $TiAl_2$ and Ti_2Al_5 in rich aluminum content can be explained as above.

4 CALCULATION OF HIGH LIQUIDUS TEMPERATURES WITH IIs

Theoretical liquidus temperatures can be obtained by calculating formation enthalpy and configurational entropy according to the EET and Cluster Variation Method (CVM)[12], and so can liquidus temperatures be affected by IIs, but during calculating, corresponding bond parameters of crystal with IIs should be taken into the formation enthalpy equation of phase equilibria because of "melting nucleus mechanism" as after. It is emphasized that there is an II atom in every crystal lattice in this instance, and its solubility is much more than that of real alloys. So, liquidus temperatures finally obtained should be linearly revised according to the solubility of the specific phase with an II atom and real one averagely estimated.

Finally, liquidus temperatures are obtained from calculating results[12] as shown in Fig.1. The liquidus temperatures affected by IIs are less than that of the alloy phase without IIs. It can be explained that phase transformation as melting and crystallizing is accomplished generally by nucleation and growth, and nucleation arises at the location where distortion energy is high. Crystal lattice with IIs is a nucleation location because of the little variation of main bonds affected by IIs so that the whole phase transformation may be influenced naturally. It can be concluded that melting arises in crystal lattice with IIs at the temperature which is less than melting point of the alloy phase without IIs, i.e. heat force can break concentrically main bonds affected by IIs and form a "melting nucleus", and then break in order other main bonds of crystal lattice without IIs, which results in melting growth. It is predicted that the heat activation energy will become very small as the "melting nucleus" increases and grows, and then liquidus temperatures affected by the IIs are lower than that of alloy phase without IIs. It is emphasized that ideal monocrystal is discussed here. For the real polycrystal, crystal interfaces of crystal lattice with IIs have priority to nucleation.

Two experimental curves are shown in Fig.1 too. Generally speaking, authoritative Ti-Al phase diagrams are obtained by Murray who reckoned comprehensively experimental results before 1987. The calculated liquidus temperatures without IIs in this article are higher than those of Murray by average 70 ℃ or so, and calculated liquidus temperatures with IIs are lower

than those without IIs by average 80 ℃ or so and by maximum 100 ℃, which is near Murray's liquidus temperatures. So, the reason why Murray's liquidus temperatures are very low is that the serious effect of IIs is not controlled in experimental determination. In fact, Anderson *et al* has strictly controlled effect of IIs by an electromagnetic levitation technique in their novel experiment, and their liquidus temperatures are similar to ours. As also shown in Fig.1, liquidus temperature in approximate 50 % Al(mole fraction) alloy is the lowest. This is because the phase transformation is complicated, the transformation temperature field is narrow in this composition region, and IIs make bond structure seriously anisotropic, which hinders some transformation and makes liquidus curves move intensely to low temperature regions.

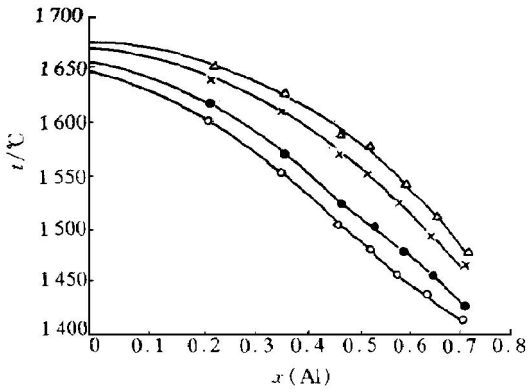

Fig.1 Calculated and experimental liquidus curves in Ti-Al phase diagram
△ —Calculated values without IIs;
× —Anderson's experimental values;
● —Murray's experimental values;
○ —Calculated values with IIs

5 CALCULATION OF MELTING POINTS WITH IIs

5.1 Calculation model

According to the EET, crystal with d electrons will melt when the temperature is high enough to form 3 Nk phonons in N atoms and make 3 $NkT = U_B$, i.e.

$$T_m = U_B/(3kN) = U_B/(3R)$$

where T_m is the melting point temperature of crystal, K; U_B is the bond energy of the strongest bond; R is the gas constant; k is Boltzman's constant.

Incorporating it into bond energy formula of high temperatures, the formula of melting point of crystal with d electrons can be written as

$$T_m = \frac{b}{3R}\{\frac{n_A}{D_{(nA)}}f + \frac{n_1}{D \cdot I_s}f' - \frac{CW}{I_s}\} \times 10^3$$

where 10^3 is drawn to unify the unit of various parameters. Incorporating corresponding parameters of the strongest bond of β, α or γ phase respectively into the formula, we can obtain theoretic values of melting point temperatures of these phases. Corresponding parameters of alloy phases with IIs must be incorporated into the formula, and similarly, obtained melting points temperatures can be linearly revised according to the real solubility of IIs.

5.2 Calculated results and discussion

The calculated results are listed in Table 4. As indicated in Table 4, the calculated transformation temperatures of alloy phases without IIs are higher than the experimental ones, and the calculated values with IIs are far lower than those without IIs, which agrees with the effects of IIs on liqudus curves at high temperatures. Also, as seen in Table 4, descendant degree of the melting point is much larger than that of the allotropism because of the effect of IIs. It is known from the above-analysed VESs that IIs weaken the main bonds of α and β phases. However, being similar to that of melting points, the calculation in this article only deals with the main bonds of α phase being weakened so that the calculated transformation temperatur-

Table 4 Experimental and calculated transformation temperatures

Transformation	Experimental value / K	Calculated value / K	Calculated value with IIs/ K
$\beta \rightarrow L$(Melting)	1 943	2 093	1 894
$\alpha \rightarrow \beta$(Allotropism)	1 155	1 206	1 121
$\gamma \rightarrow L$(Melting)	1 735	1 859	1 690

res obviously decrease.

6 SUMMARY

As indicated from the analyses and calculated results, many important and doubtful experimental results of phase transformation in Ti-Al alloys can be explained rationally by approximate dealing according to the Average Crystal lattice and Atom Model of EET, and some quantitative results can be obtained. However, limitations or questions of the dealing should be explained by the analyses and calculated results in order to improve the suceessive work.

(1) It is thought that IIs exist in the form of solid solution but not in compound because the content of IIs in real alloys is very low.

(2) It is also thought that IIs have no or negligible effect on liquid phase because the action between atoms in liquid phase is weaker than that in solid phase, and the variation of bond structures of solid phases affected by IIs is naturally different from that of liquid phases.

(3) Entropy of crystal increases very largely if a small amount of IIs is dissolved in crystal[13]. However, whether melting or crystallizing is related to liquidus phase equilibria, IIs weaken the main bonds of solid phases and make a "nucleating" mechanism operate, and then the effect of IIs on enthalpy of solid phases is analogous to a "stress concentration", and the average or statistical effect of IIs on entropy is smaller than that of IIs on enthalpy. So, it can be thought that IIs only affect enthalpy and not entropy of solid phases.

Based on the three approximations, we quantitatively dealed with the phase equilibria related to liquid phase. However, it is difficult to deal with the phase equilibria between solid phases because IIs affect every solid phase similarly, and quantative results are in calculation error and not rational.

(4) "Linear revision" of "average IIs" and real solubility is used for simplifying calculation. However, as indicated in Table 4, the difference value between calculated temperatures with IIs and without IIs is 169 K because contents of every kind of IIs and those in real crystal are different, and the deviation is very large. This is obviously because the approximations excessively simplify real circumstances, but as quantative estimation, the calculated results in this article are still rational and really significant.

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