

Influence of interstitial impurities on the valence electron structures and phase transformation behavior in intermediate Ti–Al alloys

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Abstract Development of intermetallic compounds in Ti–Al alloys for high-temperature structural applications has long been impeded due to their embrittlement. To overcome the embrittlement, it is necessary to understand thoroughly its chemical bonding nature and the resultant phase transformation behavior. In this study, based on the Empirical Electron Theory of Solids and Molecules (EET), effects of interstitial impurities on the valence electron structures and phase transformations in the intermediate Ti–Al alloys were investigated. It was demonstrated that for such alloy systems, because interstitial impurities can enhance the hybridization states of Ti and Al atoms, the valence electron structures of various phases became considerably anisotropic. As a result, some phase transformations at high temperatures was hindered, leading to the occurrence of complex metastable phases at the room

temperature. Such theoretical calculations clarified some unclear results from experimental observations in the literature.

Introduction

The intermetallic compounds in Ti–Al alloys have received considerable attention as candidate materials for relatively high temperature uses such as turbine engine components. The major disadvantages of these materials are their low ductility and toughness at room temperatures. Considerable improvements on these properties have been achieved by alloying and thermal mechanical processing [1, 2]. However, the complete success on the elimination of the embrittlement has never been reached due to the lack of a thorough understanding on the phase transformation behavior in this alloy system. In particular, the relationships between the intermediate phases have been the subject of considerable debate in the past decades. It was indicated that besides the accuracy in experimental observations and the limitation in measuring techniques, the strong interactions between different interstitial impurities (IIs) such as O, N, C, H and Ti, Al atoms affect dramatically the transformation behavior in Ti–Al alloys [3–6]. For example, a small amount of IIs can result in the concurrence of unclear or uncertain phases, implying a shift in the position of the phase boundaries of an equilibrium diagram. This therefore makes it difficult to achieve a completely satisfactory phase diagram in this system. Surprisingly however, various studies on the phase transformation in Ti–Al alloys hardly involved the important effect of IIs; quantitative results, in particular, based on theoretical analysis were never reported in the literature. The main reason for this is that essentially, phase transformation

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behavior should be attributed to chemical bond nature or electronic structures. For a fundamental understanding, it is necessary to obtain electronic structures; however, this has never been easy matter. In principle, electronic structures can be calculated using first-principles (e.g., local density functional (LDF) method [7–9]). In practice, however, such calculations are not only physically difficult, but also computationally expensive, in particular, for studies of the effect of IIs in a complex alloy system.

The Empirical Electron Theory of Solids and Molecules (EET), which was first proposed and further developed by Yu [10], provides a concise and practical Bond Length Difference (BLD) method to calculate electron structures and is especially suitable for the study of such a complex alloy system with various IIs. The foundation of EET is based on an inductive approach. It took more than 30 years from the beginning of its theoretical research to publication. The main reason is that EET must be subject to many modern theories (such as energy band, covalent bond, and Home-Rothery's electron concentration) and experimental results (such as neutron scattering, electron diffraction, microwave, Mossbauer effect, spin resonance, positron annihilation, and Compton scattering) to corroborate its applicability. Over the past decades, Yu and the subsequent researchers [11] had analyzed and summarized a number of modern experimental results, 78 elements in the periodic table of the first six periods in the periodic table of elements (except for rare gases), thousands of crystalline and molecular structures, alloy phase diagrams, and a series of data on physical properties to check and systemize EET. It was found that under first-order approximation, the calculated and analyzed results of EET agree with experiment. Since the EET was published in 1978, more than 10 branches (such as mechanics, thermodynamics (e.g., melting point, boiling point, coefficient of linear expansion, cohesive energy of elements, alloys and compounds, thermal conductivity), electromagnetics (e.g., electron conductivity, magnetic moment and high temperature superconductivity), binary alloys phase diagrams and phase transitions, and high compression phase transitions) have been formed and continued to rapidly develop. The main body of EET was based on Pauling's electron theory of metals and the quantum theory. The general conclusions drawn from the investigation were summarized in three hypotheses and a special computational method. For detailed information on the method and further procedures for the calculation of valence electron structures, refer to [12–15]. In this study, according to the method and the Average Crystal Lattice and Atom Model of the EET, the valence electron structures (VES) of Ti–Al alloys with and without of IIs were analyzed. Based on the calculated results, the effect of IIs on the transformation behavior

was investigated and some unclear experimental results in the literature were further explained.

Analysis of VESs by the BLD method

VESs of various phases in Ti–Al alloys without IIs

In Ti–Al alloys, stable phases mainly includes α -Ti, β -Ti, Ti₃Al (α_2), TiAl (γ), TiAl₃ and pure Al. The VESs of these phases have been analyzed in detail based on the BLD method of the EET. The calculated results are listed in Table 1 [16].

VESs of various phases in Ti–Al alloys with IIs

VESs of solid solution phases with O, N, C and H can be calculated using the same procedure based on the Average Crystal Lattice Model of the EET [10, 11]. However, here it should be indicated that because of the low solubility of IIs into Ti–Al alloys (also see below), the interstitial solid solution may be thought as an ideal mixture of crystal lattices with and without interstitial impurity atoms. Thus, present study will mainly focus on the VESs of various crystal lattices with IIs since the VESs without IIs have been well documented before [16]. For the calculation of

Table 1 VESs of various phases in Ti–Al system without IIs

Material	Constants	Bond	I_x	n_x
β -Ti	$a = 0.3313$ nm	A	8	0.2806
	$\sigma_{Ti} = A10$	B	6	0.0513
α -Ti	$a = 0.2950$ nm	A	6	0.2472
	$c = 0.4688$ nm	B	6	0.2070
	$\sigma_{Ti} = A10$	C	6	0.0045
Ti ₃ Al	$a = 0.5782$ nm	A	12	0.2560
	$c = 0.4629$ nm	B	12	0.2440
	$\sigma_{Ti} = A13$	C	12	0.2296
	$\sigma_{Al} = A4$	D	12	0.2198
TiAl	$a = 0.4005$ nm	A	4	0.2559
	$c = 0.4070$ nm	B	4	0.2375
	$\sigma_{Ti} = A14$	C	16	0.2283
	$\sigma_{Al}=A4$	D	4	0.0053
TiAl ₃	$a = 0.3843$ nm	A	8	0.3316
	$c = 0.8596$ nm	B	8	0.3177
	$\sigma_{Ti} = A14$	C	16	0.1676
	$\sigma_{Al} = A4$	D	16	0.1750
Al	$a = 0.4049$ nm	A	12	0.2086
	$\sigma_{Al} = A4$	B	6	0.0045

a, c —Lattice constants; σ —hybridization state; I_x —bond numbers; n_x —covalent electron numbers

the VESs of various crystal lattices with IIs, the following issues on the crystal lattice with IIs should be addressed.

(1) *Positions of IIs*

O, N, C and H should locate in the largest interstitial positions of every crystal lattice. For α -Ti, its crystal structure and most interstitial positions are A3 and octahedron, respectively; for β -Ti, they are A2 and tetrahedron, respectively; for γ , they are L₁₀ and approximate tetrahedron, respectively; for α_2 , they are DO₁₉ and approximate octahedron, respectively; and for TiAl₃, they are DO₂₂ and approximate tetrahedron, respectively.

(2) *Solubility of IIs*

Ti–Al alloys are very susceptible to IIs, but it is known from Refs. [17–19] that the real solubility of Ti–Al alloys is not more than 2.0% (mole fraction). Thus, each single crystal lattice can contain only one interstitial atom.

(3) *Lattice constant of crystal lattice with IIs*

Because the solubility of IIs is small, which results in a small distortion of the crystal lattice, the lattice constant 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 structures of solid phases are similar because of low and approximate solubility, small atom radius, 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. Therefore, to concisely and quantitatively evaluate the comprehensive effect of common IIs on the VESs, we can approximately regard O, N, C and H as a kind of equivalent “average interstitial atom” to simplify calculations, i.e., numbers of covalent and lattice electron, and single bond radii, \bar{n}_c , \bar{n}_l , and \bar{R}_l , are given by the following equations, respectively:

$$\bar{n}_c = an_c^O + bn_c^N + cn_c^C + dn_c^H \tag{1}$$

$$\bar{n}_l = an_l^O + bn_l^N + cn_l^C + dn_l^H \tag{2}$$

$$\bar{R}_l = aR_c^O + bR_c^N + cR_c^C + dR_c^H \tag{3}$$

where a , b , c and d are the proportional coefficients of real solubility of IIs, which are obtained from Refs. [17–19].

Here a few remarkable points in the above analysis should be pointed out:

- (1) It is assumed 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) IIs have no or negligible effects on liquid phase because the reaction between atoms in liquid phase is weaker than that in solid phases, and the variation of bond structures of solid phases affected by IIs is essentially different from that of liquid phases.
- (3) Entropy of crystal increases very largely if a small amount of IIs is dissolved in a crystal [20]. However, whether melting or crystallizing is related to liquids phase equilibrium, IIs can weaken the main bonds of solid phases and make a “nucleating” mechanism operate. This leads to that the effect of IIs on the enthalpy of solid phases is similar to that of a “stress concentration”, and the average or statistical effect of IIs on entropy is smaller than that of IIs on enthalpy. Thus, it can be believed that IIs only affect enthalpy and have no effect on the entropy of solid phases.
- (4) “Linear revision” of “average IIs” and real solubility is used for simplifying calculations. This approximation may excessively simplify the real situation, but as a quantitative estimation it is rational; this has been supported by the following calculated results (see below).

According to the BLD method in the EET, the covalent bond length $D_{uv}(n_p)$ between u and v atoms is given by the following equation:

$$D_{uv}(n_p) = R_u - R_v - q \log n_p \tag{4}$$

where u and v atoms may or not be the same kind of atoms. n_p denotes the number of pairs of covalent electrons, which may or not be an integer. p takes the symbols A, B, ...N for the various kinds of bond D_{uv} 's in the structure. q is constant. The VESs of crystal lattice with IIs were calculated by the method. The results are listed in Table 2.

Discussions

Effects of IIs on the VESs

As indicated in Table 2, IIs can enhance the hybridization states of Ti and Al atoms, which leads to changes in VES of crystal lattice with IIs. Generally, the strongest bond of crystal lattice with IIs is formed between IIs and metal atoms where the number of covalent electron is much more than that without IIs, while A', B' and C' bonds formed between Ti and Al atoms are weakened by IIs, and their

Table 2 VESs of various phases Ti–Al system with average IIs

Material	Constants	Bond	I_α	n_α
α -Ti	$\sigma_{\text{Ti}} = \text{A13}, \sigma_{\text{Al}} = 4$	A	12	0.9186
	$\sigma_{\text{O}} = 2, \sigma_{\text{N}} = 1$	A'	18	0.1586
	$\sigma_{\text{C}} = 6, \sigma_{\text{H}} = \text{A4}$	B'	18	0.0943
β -Ti	$\sigma_{\text{Ti}}^{\text{I}} = \text{A13}, \sigma_{\text{Ti}}^{\text{II}} = \text{A14}$	A	4	0.8761
	$\sigma_{\text{Al}} = 4, \sigma_{\text{O}} = 2$	A'	16	0.1941
	$\sigma_{\text{N}} = 1, \sigma_{\text{C}} = 6, \sigma_{\text{H}} = \text{A4}$	B'	16	0.0431
TiAl	$\sigma_{\text{Ti}}^{\text{I}} = \text{A16}, \sigma_{\text{Ti}}^{\text{II}} = \text{A17}$	A	8	0.9761
	$\sigma_{\text{Al}} = 5, \sigma_{\text{O}} = 2$	A'	8	0.1461
	$\sigma_{\text{N}} = 1, \sigma_{\text{C}} = 6,$ $\sigma_{\text{H}} = \text{A4}$	B'	8	0.1374
Ti ₃ Al	$\sigma_{\text{Ti}} = \text{A16}, \sigma_{\text{Al}} = 5$	A	12	0.9236
	$\sigma_{\text{O}} = 2, \sigma_{\text{N}} = 1$	A'	12	0.1470
	$\sigma_{\text{C}} = 6, \sigma_{\text{H}} = \text{A4}$	B'	12	0.1230
TiAl ₃	$\sigma_{\text{Ti}} = \text{A17}, \sigma_{\text{Al}} = 5$	A	8	1.2305
	$\sigma_{\text{O}} = 2, \sigma_{\text{N}} = 1$	A'	16	0.2894
	$\sigma_{\text{C}} = 6, \sigma_{\text{H}} = \text{A4}$	B'	16	0.2819
		C'	32	0.1568

A is the strongest bond, and A', B' and C' are the bonds corresponding to A, B and C of crystal lattice without IIs, respectively

numbers of covalent electrons are decreased. At the same time, the number of lattice electrons of a crystal lattice with IIs is also decreased very much. From the above results, we conclude that IIs make the bonds stronger in some directions and weaker in others, implying a quiet anisotropic bonding structure. Because of the difference in crystalline and bond structure of the different phases, the difference in the effects of IIs is very large. Generally, original A and B bonds of α -Ti and β -Ti are weakened most dramatically, followed by those of Ti₃Al and TiAl, whereas those of TiAl₃ are affected most slightly. Furthermore, if comparing the VESs of solidified α -Ti with β -Ti as well as ordered Ti₃Al with TiAl, there is a little difference in bond structures. However, it is the difference, especially with cooperation with the effects of compositions and temperature, that results in very seriously anisotropic bond structures in these phases, which may further affect the corresponding phase transformations. This is the essential reason why IIs affect phase transformation in Ti–Al alloys. A profound understanding depends on specific phases and the external conditions as discussed below.

Effects of IIs on the invariant reactions

According to the EET, the effect of IIs on bond structures can be reflected by comparing the main bonds such as A' and B' with IIs to the corresponding bonds without IIs. The main bond energies of α -Ti and β -Ti can be calculated by

Table 3 Descendant degrees of bond energy with IIs.

E	Bond energy	Bond energy with IIs	Descendant degree
$E_\alpha/(\text{kJ mol}^{-1})$	24.176	21.894	9.44%
$E_\beta/(\text{kJ mol}^{-1})$	28.435	26.213	7.81%

the bond energy formula of the EET [11]. The calculated results are illustrated in Table 3. As seen, the bond energy of α -Ti decreases more greatly than that of β -Ti, which makes the stability of this alloy system lower and hinders allotropic transformation $\alpha \rightarrow \beta$. Meanwhile, as seen in Table 2, IIs also make the VES of β -Ti more stable than that of α -Ti at $\beta \rightarrow \alpha$. As a result, the reconstruction transformation, in which crystal structure of β -Ti is broken to form that of α -Ti, is restrained, i.e., IIs play a crucial role in stabilizing β -Ti and hindering $\beta \rightarrow \alpha$ transformation. Such a mechanism is similar to that employed for hydrogen as a temporary element to form β phase at the room temperature and to increase the toughness of Ti–aluminides in the literature [3–6]. Based on this mechanism, we can analyze the phase transformation in intermediate Ti–Al alloys. It is expected that the two peritectics reactions $L + \beta \rightarrow \alpha$ and $L + \alpha \rightarrow \gamma$ should occur at high temperatures as demonstrated by McCullough et al. [3]. However, the two reactions actually hardly occur because of the locking effect of IIs on the VES of β -Ti, implying an over-stable β -phase. As a result, L₁₀ crystal structure of ordered γ phase similar to that of β phase can be produced finally as the temperature decreases. This is the essentially thermodynamic reason why there is only one peritectics $L + \beta \rightarrow \gamma$ in Murray's Ti–Al phase diagrams [4]. Similarly, uncertain experimental results on α_2/α phase boundary and invariant reaction $\alpha_2 + \gamma \rightarrow \alpha$ can be explained based on the above analyses.

Effect of IIs on metastable phases

The crystal structure of metastable phase Ti₂Al is similar to that of α_2 , which is an intermediate phase during the phase transformation from α_2 to γ , i.e., the transformation of $\alpha \rightarrow \text{Ti}_2\text{Al} \rightarrow \gamma$ arises and obeys the crystal orientation relations as follows [5]:

$$[011]_\gamma // [1\bar{1}\bar{2}0]_{\text{Ti}_2\text{Al}} // [1\bar{1}\bar{2}0]_{\alpha_2}, \quad (5)$$

and

$$(011)_\gamma // (0001)_{\text{Ti}_2\text{Al}} // (0001)_{\alpha_2} \quad (6)$$

Therefore, the transformation from α_2 to Ti₂Al is a typical one of displacement, and Ti₂Al to γ is one of reconstruction. If the kinetic condition is ideal, Ti₂Al phase

will be hardly left during a complete transformation process from α_2 to γ . However, as shown in Table 2, because the main bonds A', B' and C' of α_2 phase are weakened more considerably than those of γ phase due to IIs, the stability of α_2 will be lower than that of γ . As a result, the reconstruction transformation of Ti_2Al to γ is hindered relatively. At the same time, because the displacement transformation from α_2 to Ti_2Al does not need to break main bonds, the transformation can arise easily since the locking effect of IIs is very weak. Therefore, due to IIs, especially, for a favorable kinetic condition such as a quick cooling, the metastable phase Ti_2Al is easy to form during an incomplete transformation from α_2 to γ and even exists at the room temperature. Similarly, the occurrence of metastable phase TiAl_2 or Ti_2Al_5 in rich aluminum content can also be explained as above.

Conclusion

Research has been conducted to investigate effects of IIs on valence electron structures and phase transformations in the intermediate Ti–Al alloys based on the EET. The results show that IIs make atom states increased and valence electron structures considerably anisotropic. Because of the above change in bonding structures, the main phase transformation such as $\beta \rightarrow \alpha$ was hindered,

leading to the occurrence of various complex metastable phases.

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