PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Site preference of ternary additions in γ-TiAl: A density-functional cluster-model study

Yang Jinlong
Chinese Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing 100080, People's Republic of China and Center for Fundamental Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Xiao Chuanyun
Department of Physics, Huazhong Normal University, Wuhan, Hubei 430070, People's Republic of China

Xia Shangda
Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Wang Kelin
Center for Fundamental Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

(Received 20 July 1992)

The site preference of ternary additions Mg, V, Cr, Mn, Ga, and Mo in γ-TiAl intermetallic compounds is studied using the discrete-variational local-density-functional method with cluster models. The relations of the site preference of ternary additions with the compositions of the host elements and with the concentrations of the additions themselves in the host are obtained. The results explain satisfactorily the experimental observations and are discussed with the effects of ternary additions in improving the ductility of γ-TiAl.

I. INTRODUCTION

As one of the most promising high-temperature structural materials, γ-TiAl has been a subject of widespread investigation.$^{1-6}$ γ-TiAl is an intermetallic compound with an L_{10}-type structure ($a=3.999$ Å, $c/a=1.02$).^{1} This type structure is based on an ordered fcc tetragonal cell in which the Ti and Al atoms occupy alternating (002) planes.^{2} γ-TiAl can exist stably in a nonstoichiometric compositional range of about 40 at % to 60 at % Al, and has many attractive properties, such as a low-density, high melting point, high modulus, and good oxidation resistance.^{3,4} Unfortunately, it suffers from poor ductility at room temperature, which has so far prevented it from practical use.^{5,6} Recently, alloying additions of V, Mn, or Cr have been reported to result in increased ductility.$^{7-10}$

For a long time, there has been an attempt to correlate the mechanical properties of materials with their electronic structures.$^{11-14}$ To obtain the results of electronic structure calculations, as the first step, one must know the microscopic structures of materials. Thus, in order to understand the effects of ternary additions in improving the ductility of γ-TiAl from the electronic structure theory, it is important to determine their occupation sites in the host. Generally speaking, the site preference of additions in an intermetallic compound can be determined directly by experiments, but only a few experimental results have been reported.^{10,15,16} Theoretically, there has not been a first-principles approach to study this problem up to now, and all the previous approaches^{17,18} are empirical or semiempirical. For the ternary site preference in γ-TiAl, an empirical study has been carried out by Nandy, Banerjee, and Gogia.^{19} These authors used a thermodynamical approach coupled with the information from the ternary phase diagrams to predict the ternary site preference in γ-TiAl. Due to the fact that the method used empirical parameters and neglected the tetragonality of structure, their results for some ternary additions are not consistent with the experimental observations. For example, they predicted that V additions prefer the Ti sites, while recent atom location by channeling-enhanced microanalysis (ALCHEMI) studies^{10} indicate that the V site preference depends on the compositions of the host elements.

In this paper, we perform first-principles binding-energy calculations to study the site preference of ternary additions in γ-TiAl. Cluster models are adopted in the calculations, which have been used successfully to study the electronic structure of impurities in metals and alloys.^{20,21} According to the structure of γ-TiAl, we choose the substitutional cluster for titanium sites, $M\mathrm{Ti}_4\mathrm{Al}_8$, as the first type of cluster, and the substitutional cluster for aluminum sites, $M\mathrm{Al}_4\mathrm{Ti}_8$, as the second type of cluster, where $M=$Al, Mg, Ti, V, Cr, Mn, Ga,

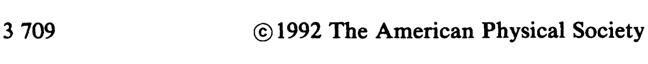

FIG. 1. Cluster models. (a) The unit cell of γ-TiAl, (b) $M\mathrm{Ti}_4\mathrm{Al}_8$ cluster, and (c) $M\mathrm{Al}_4\mathrm{Ti}_8$ cluster.

and Mo (see Fig. 1). Each of the clusters corresponds to an M atom coordinated by its first-nearest-neighbor Al and Ti atoms with D_{4h} point-group symmetry. Among these clusters, $TiTi_4Al_8$ and $AlAl_4Ti_8$ represent the Ti site and Al site local structures of the stoichiometric γ-TiAl, respectively [hereafter TiAl(s)], ($TiTi_4Al_8$, $AlTi_4Al_8$) and $AlAl_4Ti_8$ represent the Ti site and Al site local structures of the Al-rich γ-TiAl [hereafter, TiAl(r)], and $TiTi_4Ti_8$ and ($AlAl_4Ti_8$, $TiAl_4Ti_8$) represent the Ti site and Al site local structures of the Al-poor (Ti-rich) γ-TiAl [hereafter, TiAl(p)].

II. METHOD

The discrete-variational local-density-functional (DV-LDF) method is used to calculate the binding energies of the clusters. This method is a kind of molecular-orbital calculational method, and its theoretical foundation is LDF theory. Since it has been described in detail elsewhere,[22-24] here we only recall its essential features and discuss the choice of computational parameters.

The method may be summarized by seven basic points as follows:

(a) In the effective Schrödinger equation for one-particle orbitals, the usual nonlocal Hartree-Fock exchange potential is replaced by an exchange-correlation potential depending only on the local electron density $\rho(\mathbf{r})$. In this paper, the exchange-correlation potential is taken to be of the von Barth–Hedin form,[25] with the parameters taken from Moruzzi, Janak, and Williams.[26]

(b) The matrix elements of the Hamiltonian and overlap matrices are obtained by a weighted summation over a set of discrete sample points (Diophantine points) (Ref. 22) $\mathbf{r}_k$, i.e.,

$$H_{ij}=\langle \chi_i|H|\chi_j\rangle =\sum_k \omega(\mathbf{r}_k)\chi_i^*(\mathbf{r}_k)H(\mathbf{r}_k)\chi_j(\mathbf{r}_k)\ , \tag{1}$$

$$S_{ij}=\langle \chi_i|\chi_j\rangle=\sum_k \omega(\mathbf{r}_k)\chi_i^*(\mathbf{r}_k)\chi_j(\mathbf{r}_k)\ , \tag{2}$$

where $\omega(\mathbf{r}_k)$'s are appropriate integration weights. We choose 300 Diophantine points per atom for all atoms in our calculations.

(c) The calculation of Coulomb integrals is simplified by introducing the average self-consistent charge density ρ_{SCC} (SCC approximation):[23]

$$\rho=\rho_{\text{SCC}}=\sum_{vnl} f_{nl}^{v}|R_{nl}(\mathbf{r}_v)|^2\ , \tag{3}$$

where f_{nl}^{v} is the Mulliken population for the nl atomic shell of atom v, $R_{nl}(\mathbf{r}_v)$ is the corresponding radial function, evaluated at distance ($\mathbf{r}_v$) from the nuclear position.

(d) The one-electron state χ_i and energy eigenvalue ε_i are obtained through the following charge self-consistent process:

$$\begin{tikzcd} \rho_{\text{atom}} \arrow[r] & \rho_{\text{SCC}} \arrow[r] & V_c+V_{\text{xc}} \arrow[dl] \\ & \{\varepsilon_i,\chi_i\}\ . \arrow[u] & \end{tikzcd} \tag{4}$$

(e) The numerical atomic basis functions are chosen as the variational basis set, which are obtained from the self-consistent atomic LDF calculations.[27] We choose the 1s-np of an M atom (M=Al and Mg, n=3; M=Ti, V, Cr, Mn, and Ga, n=4; M=Mo, n=5) as the basis set in our calculations (hereafter, the basis set A). the lower-energy orbitals are treated as frozen cores.

(f) The total energy of a cluster is written in standard notation[24] as

$$E_{\text{tot}}=\sum_i f_i\varepsilon_i-\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+\int\rho(\mathbf{r})[\varepsilon_{\text{xc}}(\mathbf{r})-v_{\text{xc}}(\mathbf{r})]d\mathbf{r}+\tfrac{1}{2}\sum_\mu\sum_v{}'\frac{Z_\mu Z_v}{R_{\mu v}}\ , \tag{5}$$

where f_i is the Fermi-Dirac occupation number and ε_{xc} and v_{xc} are, respectively, the exchange-correlation energy density and potential in the LDF approximation. The binding energy of the cluster is then defined with respect to some reference system, say, the dissociated atoms, as

$$E_b=-(E_{\text{tot}}-E_{\text{tot}}^{\text{ref}})\ . \tag{6}$$

The substitutional ways for ternary additions to occupy the same kind of sites are different in TiAl(s), TiAl(r), and TiAl(p). In TiAl(s), the ternary additions occupy the Ti(Al) sites by substituting for Ti(Al) atoms only. However, they can locate in the Ti sites of TiAl(r) and the Al sites of TiAl(p) by substituting for either Ti or Al atoms. Hence, we define four energy parameters ΔE_i(i=1,2,3,4) for each M as follows:

$$\Delta E_1=E_b(MTi_4Al_8)-E_b(TiTi_4Al_8)\ , \tag{7}$$

$$\Delta E_2=E_b(MTi_4Al_8)-E_b(AlTi_4Al_8)\ , \tag{8}$$

$$\Delta E_3=E_b(MAl_4Ti_8)-E_b(AlAl_4Ti_8)\ , \tag{9}$$

$$\Delta E_4=E_b(MAl_4Ti_8)-E_b(TiAl_4Ti_8)\ . \tag{10}$$

ΔE_i here is somewhat like the formation energy of an impurity in the host.[28] According to the lowest energy principle, we can determine the site preference of each M in γ-TiAl by comparing the values of ΔE_i.

We have estimated the accuracy of our method. The convergence of the basis set was examined by performing cluster calculations using the basis set B, which includes the nd of an M atom based on the basis set A. We found that there is a small difference between E_b (basis set A) and E_b (basis set B), but the values of ΔE_i calculated by using E_b (basis set A) and E_b (basis set B), respectively, are almost the same. Due to the fact that we are only interested in the comparison of the ΔE_i values, in this sense we can say that the basis set A used in our calculations is convergent. As for the number of integration points, it was found that 300 Diophantine points per atom (or total 3900 numerical integration points for a cluster) in both the self-consistent field (SCF) and energy procedures, with the use of the point-by-point error-cancellation technique for E_b, were sufficient to produce an average relative precision of ± 0.05 eV in the binding energies (at this moment, the absolute errors in the total energies are of the order of 1 eV). With this degree of precision it is possible to compare the ΔE_i values for a given M. In addition, we also tested the effects of the cluster size and frozen core approximation and found that they have no influence on the final results of the paper.

III. RESULTS AND DISCUSSION

Table I lists the binding energies of the clusters. From this table, one finds that the value of E_b ($M\mathrm{Ti}_4\mathrm{Al}_8$) is smaller than that of E_b ($M\mathrm{Al}_4\mathrm{Ti}_8$) for each M we calculated. This general feature may be understood by noticing that an M atom has four titanium atoms and eight aluminum atoms as its first-nearest neighbors in the first type of cluster, while it is surrounded by four Al atoms and eight Ti atoms in the second type of cluster.

The values of ΔE_i calculated by using the results of Table I are presented in Table II. Comparing the values of ΔE_1 and ΔE_3, we can determine the site preference of each M in TiAl(s) (Table III). From Table III, we find that there are three fundamental site preference behaviors for ternary additions in TiAl(s). Mg and Ga prefer the Al sites; V, Cr, and Mn prefer the Ti sites; while Mo can occupy both the Al and Ti sites. These results are the same as those of Nandy, Banerjee, and Gogia,[19] implying that their results are valid only for TiAl(s) (see also below).

Table III also lists the ternary site preference in TiAl(r), and TiAl(p). These results are obtained by comparing the values of ΔE_1, ΔE_2, and ΔE_3 for TiAl(r), and ΔE_1, ΔE_3, and ΔE_4 for TiAl(p). The three types of occupation behaviors for ternary additions exist too in TiAl(r) and TiAl(p), but given M additions may occupy the different sites in TiAl(s), TiAl(r), and TiAl(p). We can divide the ternary additions into two groups. The first group contains Mn and Ga. Their site preference remains unchanged regardless of the host being TiAl(s), TiAl(r), or TiAl(p). The other ternary additions Mg, V, Cr, and Mo belong to the second group. Their site preference depends on the compositions of the host elements. Specifically, the site preference of Mg and Mo further depends on the concentrations of the additions themselves in the host. To show this, we take Mg as an example. The composition formula for Mg alloying in TiAl(r) can be written as $\mathrm{Ti}_{50-x}\mathrm{Al}_{(50-y_1)+(x-y_2)}\,\mathrm{Mg}_y$ with $x>0$ and $y_1+y_2=y$. In this formula, Al atoms are divided into two parts: $(50-y_1)$ at % Al atoms are in the Al sites and $(x-y_2)$ at % Al atoms are in the Ti sites. From Table II, we have $\Delta E_1<\Delta E_3<\Delta E_2$ for Mg. This condition indicates that, $y_1=0$ when $y\le x$, and $y_1\neq 0$, $y_2\neq 0$ when $y>x$. This is to say that Mg only occupies the Ti site when $y\le x$ and locates in both the Ti site and Al site when $y>x$.

TABLE II. The values of ΔE_i ($i=1,2,3,4$) (eV).

M	ΔE_1	ΔE_2	ΔE_3	ΔE_4
Al	−2.17	0	0	0.31
Mg	−4.00	−1.82	−2.18	−1.87
Ti	0	2.18	−0.31	0
V	1.32	3.50	−1.02	1.33
Cr	3.36	5.54	3.00	3.31
Mn	2.00	4.18	0.87	1.17
Ga	−2.10	0.08	0.62	0.92
Mo	4.56	6.73	4.54	4.84

There are different conjectures for the Mn site preference in γ-TiAl. Tsujimoto and Hashimota[29] speculate that Mn additions mainly occupy the Al sites and thus weaken the covalency of Ti—Al bonds to enhance the ductility of γ-TiAl. Coletti *et al.*[30] infer Mn occupying the Ti site for explaining their experimental result that Mn in γ-TiAl has a localized moment that is essentially independent of Mn concentration under the condition of low dopings. A recent study[16] of the relative variation of the superlattice peak in the x-ray diffraction of the $\mathrm{Ti}_{50-x}\mathrm{Mn}_x\mathrm{Al}_{50}$ system with different Mn dopings indicates that the Mn additions occupy the Ti sites in TiAl(s). Our results exclude the possibility of Mn occupying the Al site, however, it does not mean that Mn has no effect in weakening the Ti—Al bonds. In fact, Mn additions occupy the Ti sites first by substituting for the Al atoms of the Ti sites in TiAl(r) (Table II). From our results, one can expect that the effects of Mn additions in improving the ductility of the host may have some differences in TiAl(r) and in TiAl(s) and TiAl(p).

With the technique of ALCHEMI, Huang and Hall[10] observed experimentally that V atoms occupy both the Ti

TABLE I. Binding energies of clusters (eV).

M	$E_b(M\mathrm{Ti}_4\mathrm{Al}_8)$	E_b $(M\mathrm{Al}_4\mathrm{Ti}_8)$
Al	43.21	49.60
Mg	41.38	47.42
Ti	45.38	49.29
V	46.70	50.62
Cr	48.75	52.60
Mn	47.39	50.46
Ga	43.29	50.21
Mo	49.94	54.13

TABLE III. The site preference of some ternary additions in γ-TiAl.

M	TiAl(s)	TiAl(r)	TiAl(p)
Al	Al	Al,Ti	Al
Mg	Al	Ti,(Al)	Al
Ti	Ti	Ti	Ti,Al
V	Ti	Ti	Ti,Al
Cr	Ti	Ti	Ti,Al
Mn	Ti	Ti	Ti
Ga	Al	Al	Al
Mo	Ti,Al	Ti,(Al)	Al,(Ti)

and Al sites in duplex TiAl alloys, and occupy only the Ti sites in single-phase γ-TiAl alloys. According to the Ti-Al phase diagram,[6] the single-phase γ-TiAl can be obtained only in the form of TiAl(r), and the duplex TiAl alloys are formed in the region of TiAl(p). So, our theoretical calculations reproduce their experiments very well. The results in Table II further show that V has the same behavior as Mn in TiAl(s) and TiAl(r). In TiAl(p), V can occupy the Al site, but it should have no effect in weakening the Ti—Al bonds because it locates in the Al site by the substituting for Ti of the Al site.

Our results for the Ga site preference in γ-TiAl is also consistent with the experiments.[5] For the site preference of Mg, Cr, and Mo, no experimental result is available. According to our results, Cr has the same site preference as V, indicating that it may have the same mechanism in increasing the ductility of γ-TiAl.

IV. CONCLUSIONS

We have determined the site preference of some ternary additions in γ-TiAl by the first-principles binding-energy calculations using cluster models. The calculated results clearly show how the site preference of ternary additions change with the compositions of the host elements and with the concentrations of the additions themselves in the host, and explain satisfactorily the experimental observations. They also provide a basis for further studying the effects of ternary additions in improving the ductility of γ-TiAl.

Since the method used here is of general applicability, we believe that it will become a promising tool for theoretical studies of the site preference of ternary additions in intermetallic compounds with either stoichiometic or nonstoichiometic compositions. Certainly, we should point out that the temperature effect has not been included in the present scheme for it has a very small influence on the site preference of ternary additions.[17] If necessary, however, we could use our method incorporating the cluster variation method (Ref. 31) to study the site preference at finite temperatures.

ACKNOWLEDGMENTS

We would like to thank Dr. Wan Shaolong for his technical assistance in preparing the manuscript. This work was supported by the Youth Natural Science Foundation of USTC.

---

[1] E. S. Bumps, H. D. Kessler, and M. Hansen, Trans. AIME **194**, 609 (1952).

[2] J. B. McAndrew and H. D. Kessler, J. Met. **8**, 1348 (1956).

[3] H. A. Lipsitt, Mater. Res. Soc. Symp. Proc. **39**, 351 (1985).

[4] S. R. Chubb, D. A. Papaconstantopoulos, and B. M. Klein, Phys. Rev. B **38**, 12 120 (1988).

[5] *Proceedings of the Symposium on High-temperature Ordered Intermetallic Alloys III*, edited by C. T. Liu, A. I. Taub, N. S. Stoloff, and C. C. Koch (Materials Research Society, Pittsburgh, PA, 1989).

[6] S. C. Huang and E. L. Hall, Metall. Trans. A **22**, 427 (1991).

[7] T. Hanamura, R. Uemori, and M. Tanino, J. Mater. Res. **3**, 656 (1988).

[8] S. C. Huang and E. L. Hall, Mater. Res. Soc. Symp. Proc. **133**, 373 (1989).

[9] Y. W. Kim, J. Met. **41**, 24 (1989).

[10] S. C. Huang and E. L. Hall, Acta Metall. Mater. **39**, 1053 (1991).

[11] H. L. Frisch and J. R. Patel, Phys. Rev. Lett. **18**, 784 (1967).

[12] M. S. Daw and M. I. Baskas, Phys. Rev. Lett. **50**, 1285 (1983).

[13] M. E. Eberhart and D. D. Vvendensky, Phys. Rev. Lett. **58**, 61 (1987); Phys. Rev. B **37**, 8458 (1988).

[14] G. S. Painter and F. W. Averill, Phys. Rev. Lett. **58**, 234 (1987).

[15] A. Chiba, D. Shindo, and S. Hanada, Acta Metall. Mater. **39**, 13 (1991).

[16] V. S. Babu and M. S. Seehra, J. Mater. Res. **6**, 339 (1991).

[17] S. Ochiai, Y. Oya, and T. Suzuki, Acta Metall. **32**, 289 (1984).

[18] Y. P. Wu, N. C. Tso, J. M. Scanchez, and J. K. Tien, Acta Metall. **37**, 2835 (1989).

[19] T. K. Nandy, D. Banerjee, and A. K. Gogia, Scr. Metall. Mater. **24**, 2019 (1990).

[20] Yang Jinlong, Wang Kelin, L. F. Doná dalle Rose, and F. Toigo, Phys. Rev. B **44**, 4275 (1991); **44**, 10 508 (1991).

[21] D. Guenzburger and D. E. Ellis, Phys. Rev. Lett. **67**, 3832 (1991).

[22] G. S. Painter and D. E. Ellis, Phys. Rev. B **1**, 4747 (1970).

[23] A. Rosen, D. E. Ellis, H. Adachi, and F. W. Averill, J. Chem. Phys. **65**, 3629 (1976).

[24] B. Delley, D. E. Ellis, A. J. Freeman, E. J. Baerends, and D. Post, Phys. Rev. B **27**, 2132 (1983).

[25] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[26] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[27] F. W. Averill and D. E. Ellis, J. Chem. Phys. **59**, 6412 (1973).

[28] S. A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, Phys. Rev. Lett. **66**, 2010 (1991).

[29] T. Tsujimoto and K. Hashimoto, Mater. Res. Soc. Symp. Proc. **133**, 391 (1989).

[30] J. Coletti, V. S. Babu, A. S. Pavlovic, and M. S. Seehra, Phys. Rev. B **42**, 10 754 (1990).

[31] R. Kikuchi, Phys. Rev. **81**, 988 (1951).