

Electronic structure of edge dislocation of core-doped Ti in Fe

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Received August 28, 2003; revised September 10, 2003

Abstract The electronic structure of an edge dislocation doped Ti lying in the (001) plane with Burgers Vector along [100] direction in body-centered cubic iron is investigated using the first principles discrete variational method (DVM) based on the density-functional theory. The binding energy, impurity formation energy, interatomic energy, Mulliken orbital populations and charge density difference are presented in this paper. By calculating the binding energy of the clean dislocation system and the Ti-doped system, it is found that the binding energy of Ti-doped dislocation system is lower than that of the clean dislocation system, which implies that the Ti-doped dislocation system is more stable than the clean dislocation system. The calculated result of the impurity formation energy predicts the trapping effect of dislocation core for Ti, which shows that Ti atom prefers to occupy the place at the dislocation core. The calculated results of the interatomic energy and the difference charge density of dislocation doped Ti system indicate that the stronger bonding formed between the Ti impurity and its neighbor Fe atoms will affect the mechanical property of edge dislocation. Considering the influence of Ti on the electronic structure and the energies, we can predict that the trace Ti in transition metal Fe with dislocation defect can give a significant contribution to the solid solution hardening effects and will influence the mechanical property of materials.

Keywords: edge dislocation, doping effect, electronic structure.

Dislocation is one of the important structural defects in crystals and closely relates to many physical and chemical processes, such as the growth of crystals, phase transformation, diffusion, plasticity deformation and fracture, etc. The geometrical property and doping effect of dislocation have great influence on mechanical characteristic of materials. The long-range elastic stress field of the dislocation has been well described by continuum medium model, however, considering the lattice effect of dislocation core, it is difficult to deal with the dislocation core region by the continuum medium model, so studies beyond the classical theory are needed. Since theoretical calculations of the dislocation core structure are still not perfect and experimental studies on atomic level need being carried out further, the calculation of electronic structure has been an important topic for the study of dislocation core.

The related investigation of Gehlen et al.^[1] indicated that the dislocation with the effective core radius about 1.25 ~ 1.65 Burgers Vector possesses local effect. The 1/2[100] screw dislocation in iron and its core structure were studied by Vitek^[2], which indicated that the screw dislocation motion closely relates

to the macroscopic deformation. In 1981, Masuda et al.^[3] studied the structure and the energy of 1/2<111>{110} and 1/2<111>{112} edge dislocation in α -Fe using a tight-binding type electronic theory, which showed that the electronic effect of the dislocation core is important in the research of dislocation core. Based on the Green's function, Wang et al.^[4] calculated the electronic structure of the system and found that the edge dislocation can result in the splitting of degenerate states of d electronic, and the movement of Fermi level. Fang and Wang^[5] discovered that the edge dislocation of the 1/2[110] (111) type in aluminum dissociates into two partials separating from each other by a distance of 9 Å. The dislocation mobility is also studied by applying a shear stress on the crystal and the corresponding shift of the Burgers vector density is observed based on the above works. The migration energy for vacancy diffusion in the dislocation core is evaluated about 0.5 eV. Using the first-principles real space tight-binding linear-muffin-tin-orbital recursion method, Kontsevoi et al.^[6] investigated the electronic structure of different types of dislocations in B2 intermetallic NiAl and bcc transition metals. In their studies an unusual localization of electronic states inside the valence band is ob-

* Supported by the Major State Basic Research Development Program of China (Grant No. 2000067102) and the National Natural Science Foundation of China (Grant No. 59971041)

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where $W(\mathbf{r}_k)$ is a weight function, and $\{\mathbf{r}_k\}$ is a discrete set of sample points.

Inserting (1) into (2), we have

$$\Delta_{ij} = \sum_k C_{ik}^* (H_{kl} - \epsilon_{kl}) C_{lj}. \quad (3)$$

To minimize the error function $\partial\Delta_{ij}/\partial C_{ik} = 0$, we can get the secular equation:

$$\sum_l (H_{kl} - \epsilon_l S_{kl}) C_{lj} = 0, \quad (4)$$

The elements of matrices for H and S are as follows:

$$H_{kl} = \sum_i W(\mathbf{r}_i) \chi_k^*(\mathbf{r}_i) H \chi_l(\mathbf{r}_i), \quad (5)$$

$$S_{kl} = \sum_i W(\mathbf{r}_i) \chi_k^*(\mathbf{r}_i) \chi_l(\mathbf{r}_i). \quad (6)$$

In this paper, the DVM is used to calculate the electronic structure and Ti-doping effect of edge dislocation.

1.3 Calculation parameters

For the calculations of the electronic structure of dislocations, the local density approximation (LDA) with the von Barth-Hedin form of the exchange-correlation potential was used. The frozen-core mode was applied to the inner atomic shell and two different single site orbitals (SSO's)^[14] were used in our calculations. One is a minimal basis (MB), which is bound to eigenstates of the isolated atom. The orbital sets of both Fe and Ti are constructed from 1s, 2s, 2p, 3s, 3p, 3d, 4s atomic orbitals (AO's). The other SSO basis is an extended basis (EB), which includes not only the above-mentioned AO's but also the 4p orbital of Fe or Ti.

2 Results and discussions

2.1 Energy calculation

The calculated results of the cohesive energy and the impurity formation energy with the [100] (001) edge dislocation core and its Ti-doped system in bcc iron are listed in Table 1. The cohesive energy of the clean edge dislocation (-5.08 eV) is lower than the value of experiment (-4.28 eV), which correlates with the local density approximation (LDA). In order to study the preferred site of Ti in bcc Fe, the impurity formation energy^[22] is introduced in this paper:

$$E_f = \frac{E_b(\text{T} + \text{IMP}) - E_b}{N}, \quad (7)$$

where $E_b(\text{T} + \text{IMP})$ and E_b are the binding energy of impurity-doped and clean edge dislocation system, re-

spectively, and N is the number of impurity. The calculated result of the impurity formation energy is consistent with the related results of others^[11].

Comparing the cohesive energy of the clean edge dislocation core system with that of doped Ti system, we found that the cohesive energy of doped Ti system is lower than that of the clean system. From the energy point of view, it shows that the dislocation-doped Ti system is more stable than the clean dislocation system. Moreover, the calculated result of the impurity formation energy predicts the trapping effect of dislocation core for Ti, which shows that Ti atom prefers to occupy the place of the dislocation core.

Table 1. Calculated results of the cohesive energy and the impurity formation energy of bcc Fe with the clean edge dislocation and the impurity-doped edge dislocation

	Clean edge dislocation system/ eV	V-doped edge dislocation system/ eV
E_c^a	-5.082727	-5.102018
E_f		-1.911104

a) $E_c = \frac{E_b}{n}$, and n is the total number of atoms in these systems.

2.2 Interatomic energy

In order to investigate the interaction between atoms, the interatomic energy between atom l and m is derived^[23~25]

$$E_{lm} = \sum_n \sum_{\beta} N_n \alpha_n^* t^{\alpha} t^{\beta} H_{\beta m \alpha l}, \quad (8)$$

where N_n is the occupation number of molecular orbital ψ_n , and $H_{\beta m \alpha l}$ is Hamiltonian matrix element connecting the atomic orbital β of atom m and the atomic orbital α of atom l.

The interatomic energies can reflect the bonding strength between atoms, some typical pairs of atoms with the variation of interatomic distance d are listed in Table 2, where E_{lm}^{dis} and $E_{lm}^{\text{dis}+\text{Ti}}$ present the interatomic energy of the clean and the doped Ti edge dislocation in bcc Fe, respectively, and $E_{lm}^{\text{dis}+\text{Ti}} - E_{lm}^{\text{dis}}$ is the variety of interatomic energy caused by the substitutional Ti impurity at the dislocation core. Moreover, we use d_{dis} and $d_{\text{dis}+\text{Ti}}$ to show the interatomic distance in different systems with the edge dislocation.

It is found that interactions between the nearest neighbor atoms such as Fe24(25), Fe(3) and the central atom Ti are strengthened after atom Fe1 is replaced by Ti. It is also found that the interatomic energies of atom pairs such as Fe3-14, Fe 76-77, Fe24-

25 and Fe28-29, as well as atom pairs at different layers such as Fe24-84 and Fe76-78, etc, are all increased. The tendency relates to the charge redistribution after doped Ti. Furthermore, the interatomic energies of atoms far from the impurity Ti changes slightly, which shows that the effect of Ti is localized. From the above results we can find that when the alloying element Ti is doped, the interatomic energy between the doped impurity and its neighbor host Fe atom increases, and the interatomic energy of the neighbor atoms between Ti and Fe atoms in different layers along the dislocation line increases too. Table 2 also shows that the interatomic energy depends on the interatomic distance. From 0.8 to 1.3 lattice constant the interatomic energy is negative and decreases gradually with the increasing of the interatomic distance. The calculated results of the interatomic energy are consistent with our calculations of the cohesive energy.

Table 2. Interatomic energy E_{lm} of different atom pairs at different interatomic distances of bcc [100] (001) edge dislocation

Atom-pairs	E_{lm}^{is}/eV	d_{is}/a_0	E_{lm}^{is+Ti}/eV	$E_{lm}^{is+Ti}-E_{lm}^{is}/eV$	d_{dis+Ti}/a_0
Fe1 (Ti)-Fe84	-1.3204	0.958688	-1.3745	-0.0541	0.960100
Fe1 (Ti)-Fe24	-1.2022	0.982495	-1.2458	-0.0436	0.985348
Fe1 (Ti)-Fe3	-0.6417	1.061820	-0.7390	-0.0973	1.069090
Fe1 (Ti)-Fe76	-1.3724	0.935153	-1.3027	0.0697	0.946244
Fe3-Fe14	-0.3629	1.062769	-0.3851	-0.0222	1.053746
Fe76-Fe77	-0.3605	1.088394	-0.4198	-0.0593	1.092315
Fe76-Fe78	-0.9719	0.999820	-0.9720	-0.0001	1.010595
Fe24-Fe25	-2.0642	0.833450	-2.1496	-0.0854	0.834520
Fe28-Fe29	-0.8718	0.971450	-0.8964	-0.0246	0.967960
Fe22-Fe92	-1.6155	0.852486	-1.6151	0.0004	0.853506
Fe24-Fe84	-1.9629	0.835998	-1.9993	-0.0364	0.838903
Fe10-Fe11	-0.6649	0.999810	-0.6394	0.0255	1.002740
Fe84-Fe86	-0.8503	0.999820	-0.8281	0.0285	1.007615

2.3 Mulliken orbital population

Information about the charge distribution can be obtained from the population analysis, which is given in Table 3. Table 3 lists the Mulliken orbital populations of the valence orbital of some particular atoms, where $Q=N-Z_{val}$ is the net number of charge occupation and Z_{val} is the number of standard charge occupation for each atom (isolated atom) state, N_0 and N are the number of charge occupation for the clean dislocation core and the doped dislocation core, and $\Delta N=N-N_0$ is the charge occupation number difference for the two systems.

From the comparison of the Mulliken populations, the charge transfer among different atoms and partial orbitals can be obtained, which is helpful to the analysis of the interatomic interaction and the in-

teratomic bonding character. The Mulliken populations of Fe1 atom and other listed Fe atoms, as well as Ti atom which replaces Fe1 are shown in table 3. Compared with the clean edge dislocation, it can be seen that Ti loses more electrons than Fe1 atom (Ti loses 0.3226e while Fe1 loses 0.0363e), and those host Fe atoms in the same layer with Ti such as Fe3 and Fe24(25) gain part of electrons. The main contribution of the charge transfer is from 4s and 4p orbitals which belong to Ti and its neighbor host Fe atoms. From Table 3 we can also find that the charge transfer between atoms in Ti-doped edge dislocation core is more than that of clean edge dislocation core, which reflects the tendency of stronger bonding in the Ti-doped dislocation system. The result is consistent with the calculated results of the interatomic energy.

Table 3. Mulliken orbital populations and charges of the impurity atoms and some host Fe atoms

Number of atoms	Clean edge dislocation system	Ti-doped edge dislocation system		
		$N_0(e)$	$N(e)$	$\Delta N(e)$
Fe1 (Ti)	3d(4d)	6.3479	2.3569	
	4s(5s)	0.7759	0.6131	
	4p(5p)	0.8399	0.7074	
Fe (3)	Q	-0.0363	-0.3226	-0.2863
	3d	6.3245	6.3250	0.0005
	4s	0.7302	0.7370	0.0068
Fe (18, 19)	4p	0.8270	0.8329	0.0059
	Q	-0.1183	-0.1051	0.0132
	3d	6.3157	6.3117	-0.0040
Fe (24, 25)	4s	0.7394	0.7362	-0.0032
	4p	0.9033	0.9102	0.0069
	Q	-0.0416	-0.0419	-0.0003
Fe (76, 77, 78, 79)	3d	6.3425	6.3408	-0.0017
	4s	0.7137	0.7332	0.0195
	4p	0.8887	0.9131	0.0244
Fe (84, 85, 86, 87)	Q	-0.0551	-0.0129	0.0422
	3d	6.3239	6.3269	0.0030
	4s	0.7969	0.8106	0.0137
Fe (84, 85, 86, 87)	4p	0.9366	0.9597	0.0231
	Q	0.0574	0.0972	0.0398
	3d	6.3198	6.3227	0.0029
Fe (84, 85, 86, 87)	4s	0.7670	0.7809	0.0139
	4p	0.9535	0.9736	0.0201
	Q	0.0403	0.0772	0.0369

2.4 The charge density difference

The charge density difference is obtained by subtracting the electron density of free atoms at the superposition from that of the cluster system, which can provide a physical insight into the bonding character and charge distribution. To have a clear picture of the charge distributions in the clean edge disloc-

tion core and its Ti-doped edge dislocation core, we present Fig. 3. and Fig. 4. to describe the valence charge density. For the clean edge dislocation system, the charge density difference is to subtract the charge density of free atoms from that of the clean dislocation cluster, which is $\Delta\rho_{\text{clean}} = \rho(\text{dislocation}) - \rho_{\text{free}}(\text{Fe})$. And for the Ti-doped system, the charge density difference is obtained by subtracting the charge density of the clean dislocation cluster, and the difference between the charge density of the free host atom and the impurity atom from that of impurity-doped dislocation cluster, i. e.

$$\Delta\rho_{\text{dopant}} = \rho(\text{dislocation} + \text{Ti}) - \rho(\text{dislocation}) - (\rho_{\text{free}}(\text{Ti}) - \rho_{\text{free}}(\text{Fe})).$$

Fig. 3 is about the clean edge dislocation core system. The charge density difference of the central plane A containing Fe1 atom is shown in Fig. 3 (a), from which we can find that the charge distributes in the intermediate triangle region among the atoms Fe1, Fe2 and Fe3. After the substitution of Ti for Fe1 atom, great change of the charge density difference will appear, as shown in Fig. 4 (a). Fig. 4 is the Ti-doped dislocation system charge density difference graphs. The central plane containing impurity

atom Ti is shown in Fig. 4 (a); two B planes ($Y = \pm 2.7a. u.$) adjacent to the central plane A in the stacking sequence along the direction [010] of dislocation line are shown in Fig. 4 (b, c). The three planes are with the stacking sequence BAB and perpendicular to the dislocation line. From these graphs the Ti-doped charge redistribution in the dislocation core can be easily seen. In Fig. 4 (a), we can see that the two Fe atoms Fe24 and Fe25 above the slip plane and the Fe3 atom below the slip plane are bonded to the impurity Ti atom, where the Ti atom loses electrons and the Fe atoms gain electrons, and the Ti-Fe possess the character of polarized bonding. We also find that the charge density in Fig. 4 (b) and Fig. 4 (c) are similar to that in Fig. 3 (b) and Fig. 3 (c), which relates to the periodicity along the dislocation line. From the above analysis we can conclude that there is more charge transfer in the layers along the dislocation line and crossing the slip plane, which can indicate the stronger interatomic bonding and thus influence the mechanical property of material. The analysis of the charge density difference is consistent with the calculations of the cohesive energy, interatomic energy, and Mulliken charge analyses.

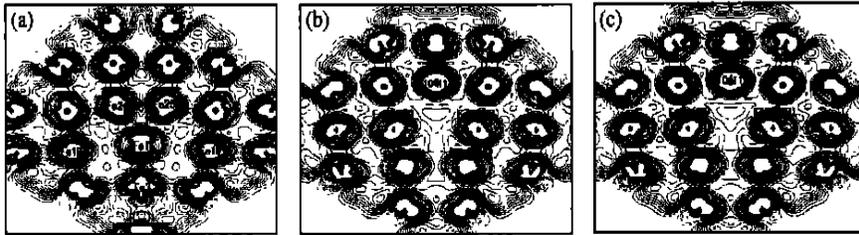


Fig. 3. Charge density difference maps about the clean edge dislocation core. (a) The central A plane ($Y=0$) containing the Fe1 atom; (b) The B plane ($Y=+2.7a. u.$) adjacent to the central plane A in the stacking sequence along the [010] direction of dislocation line; (c) The B plane ($Y=-2.7a. u.$) adjacent to the central plane A in the stacking sequence along the [010] direction of dislocation line. The solid lines and dashed lines are used to indicate the gain and the loss of electrons, respectively. The minima and maxima contours are $0.001e (a. u.)^{-3}$ and $0.02 e (a. u.)^{-3}$, and contour intervals are $0.00095e (a. u.)^{-3}$.

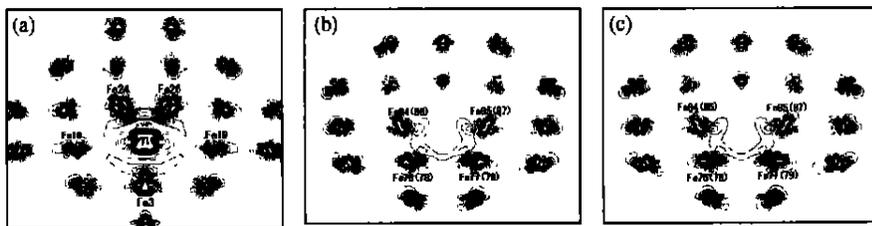


Fig. 4. Charge density difference maps about the Ti-doped edge dislocation core. (a) The central A plane ($Y=0$) containing the impurity Ti atom; (b) The B plane ($Y=+2.7a. u.$) adjacent to the central plane A in the stacking sequence along the direction [010] of dislocation line; (c) The B plane ($Y=-2.7a. u.$) adjacent to the central plane A in the stacking sequence along the [010] direction of dislocation line. The solid lines and dashed lines are used to indicate the gain and the loss of electrons, respectively. The minima and maxima contours are $0.001e (a. u.)^{-3}$ and $0.02 e (a. u.)^{-3}$, and contour intervals are $0.00095e (a. u.)^{-3}$.

3 Conclusions

In this paper, the major features of the electronic structure for the clean edge dislocation core system and its Ti-doped system have been presented using the discrete variational method (DVM). Based on the calculated results of the cohesive energy, we found that the Ti-doped edge dislocation core system in bcc Fe is relatively stable compared with the clean system. Furthermore, the calculated result of impurity formation energy demonstrates the trapping effect of dislocation core for Ti, which shows that Ti atom prefers to occupy at the dislocation core. The calculated results of the interatomic energy and the Mulliken population, as well as the analysis of the charge density difference, indicate that both the stronger interactions and the charge transfer of the Ti-doped system are more than that of the clean system. In particular, the interatomic bonding perpendicular to the dislocation line is strengthened, which relates to the dislocation-dopant effect and will influence the slip character of the edge dislocation. Based on the above calculations and analysis, we can conclude that doping of alloying element Ti in transition metal with dislocation defect has the solid solution hardening effect and may be related to the mechanical property of transition metal Fe, which is consistent with the strengthening effect of the experimental observation of doping Ti in the steel^[9, 10].

Acknowledgements The authors would like to thank Prof. Zhao Dongliang, Dr. Wang Shanying and Dr. Shang Jixiang for their help and interesting discussions in this work.

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