

First principle study of occupancy, bonding characteristics and alloying effect of Zr, Nb, V in bulk γ -Fe(C)

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Abstract. The total energy, binding characteristics, density of states, charge distribution and differential charge density of γ -Fe(C)-M crystal cells formed by solid solution of Zr, Nb and V in γ -Fe(C) were calculated by using the first-principles method. Thus, the mechanism of Zr, Nb, and V with γ -Fe(C) was investigated in this paper. The results show that Zr, Nb and V all preferentially replaced the Fe atoms which are at the top angle in γ -Fe(C). Crystal cell reaches its highest stability after V solid solution. Nb reaches after it, and Zr is relatively weak. In the γ -Fe(C)-Zr cell, Fe-Zr covalent bond and Zr-C ionic bond are the main chemical bonds. In the γ -Fe(C)-Nb and γ -Fe(C)-V cells, Fe-Nb and Fe-V covalent bonds are the main chemical bonds with a number of Nb-C and V-C ionic bonds. After solid solution, the electron cloud density around C atom changed little, while Fe atom changed obviously. The orbital electrons around Fe atoms in γ -Fe(C)-V has maximal distribution, which means that the electrons delocalized most and most of the electrons are bonding. It is the main factor for the increase in the binding energy of crystal cell. The effects of Zr, Nb, V solution on austenitic stability are investigated by studying the influence of alloy element on γ -Fe(C) electronic structure.

1 Introduction

Microalloying technology of iron/steel materials is an important method to improve its mechanical properties [1-4]. Through adding microalloying elements to steel materials, a solid solution of α -Fe(C)-M alloy was formed in order to enhance the strength. On the other hand, adding alloying elements will form a second precipitation phase with C, N or other elements, which can inhibit austenite growth and refine grains in order to improve its plasticity and toughness. Thus, the interaction between microalloying elements and austenite is an important basis for influencing the grain size of austenite, as well as one of the fundamental reasons for improving its mechanical properties. At present, domestic and foreign scholars have carried out theoretical and experimental studies on the mechanism of Ti, Cr, Nb, Mo and other elements on steel alloying [5-9], then discussed its precipitation effect on austenite grain refinement by studying the precipitation kinetics of microalloy carbonitride. Zr, Nb and V are all strong carbide forming elements, which can have a certain impact on the mechanical properties of steel. Xi tianhui et al. [10] studied the effect of Zr content on microstructure and properties of microalloyed steel. Tang xingchang et al. [2] studied the microstructure and recrystallization behaviours of Nb and Ti microalloyed low-carbon bainite high-strength steel. Gao xutao et al. [11] studied the dynamic continuous cooling phase transition of TRIP hot rolled steels, though adding Nb, V and N. Hui yajun et al. [12] studied the strengthening

mechanism of 650 MPa class V-N microalloyed high formability crossbeam steel. In recent years, relevant scholars have done lots of research works on the influence of Zr, Nb and V elements on grain refinement as well as Zr-Ti and Nb-V composite microalloying [10, 13]. Zr can easily form ZrC and ZrN with C and N, which has a significant impact on the mechanical properties of microalloyed steels. Zr can also be combined with transition group metals such as Nb, Ti, V, etc., to improve yield strength by controlling its grain size [14-15]. T.N. Baker et al. [14] found that Zr can play a role in refining austenite grains. Studies have shown that [16-17], adding Nb to steel partly instead of V can inhibit the growth of austenite grains by forming NbC at high temperature. However, the above effects on the mechanical properties of Zr, Nb and V microalloyed steels are only based on experimental and microstructure analysis, the microcosmic mechanism between the three microalloyed elements and austenite has not been further discussed from the perspective of microelectronic structure. Although Zr, Nb and V are all strong carbide forming elements, their affinity to C atom is different. So there may be some differences in the microcosmic mechanism of Zr, Nb and V on microalloying of steel. At present, there is no related research report.

Austenitic (γ -Fe(C)) is the basic phase of iron and steel materials. The effect of alloying elements on the austenitizing of steel will directly affect the stability of the austenitic, which has important guiding significance for the heat treatment process. Thus, the effect of alloying elements on the crystal structure of γ -Fe(C) has

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important theoretical and practical guiding significance for improving the microstructure and properties of austenite.

In recent years, the first-principles calculation method has been widely used in many fields such as condensed matter physics and materials science. In the reference [18], the bonding properties and alloying effects of Cr, Mo, Ni and other alloy atoms in γ -Fe alloy were analysed by first-principles calculation method. However, the interaction of Zr, Nb, V atoms with γ -Fe(C) in alloy steels is rarely discussed from the point of view of electronic structure.

In this paper, based on density functional theory, the alloying effects of Zr, Nb and V on γ -Fe(C) were studied by first principles. The microscopic mechanism of Zr, Nb and V alloy atoms interacting with γ -Fe(C) is explained in terms of electronic structure. It is expected to reveal the nature of austenitic solid solution strengthening, thus accumulate data and methods for the theoretical development of alloy design.

2 Crystal structure and Computational details

In the crystal structure of γ -Fe, the spatial point group is Fm-3m, the lattice constant is $a=b=c=3.5602 \text{ \AA}$ [18]. In this paper, a $1 \times 1 \times 2$ γ -Fe supercell model was established, and C atoms were doped in octahedral interstitials as the initial structure model of γ -Fe. On this basis, alloy atoms M (M=Zr, Nb, V) were used to displace Fe atoms in the structure model of γ -Fe(C), respectively. Substitutional solid solution models of Zr, Nb and V atoms with different placeholders in γ -Fe(C)-M were obtained, as shown in Fig. 1. Where, the purple ball represents Fe atom, the gray ball represents C atom, and the blue ball represents M alloy atom.

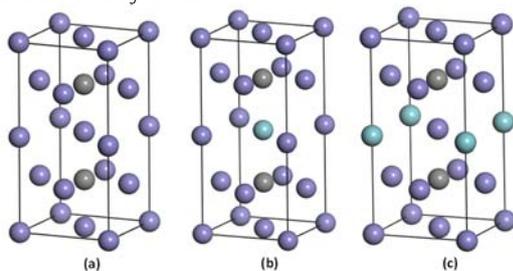


Fig. 1 Solid solution models of Zr, Nb and V atoms with different occupancy in γ -Fe(C)-M

The calculation of material structure and electronic properties adopts density functional theory (DFT) and CASTEP (Cambridge Serial Total Energy Package) software [19]. The exchange-correlation functional was approximated by generalized gradient approximation (GGA) within Perdew-Wang (PW91) scheme [20]. Ultrasoft pseudopotentials wave (USPPs) potentials [21] were used to describe Zr, Nb, and V elements and plane-wave basis set with an energy cut-off of 400eV was taken [22]. The Brillouin zone of $1 \times 1 \times 2$ super cell was sampled with $6 \times 6 \times 3$ k-point mesh set by Monkhorst-Pack method. The atomic positions were optimized by

using conjugate gradient method following the minimization of the total energy of the system. The self-consistent cycle convergence accuracy is 1.0×10^{-6} eV/atom, the total energy of self-consistent operation converges is to 1.0×10^{-5} eV/atom, the force converges to 0.01 eV/Å, respectively. The maximum number of self-consistent iteration was 200.

3 Results and discussion

3.1. The results of structural optimization and the analysis of atomic solid solution occupancy

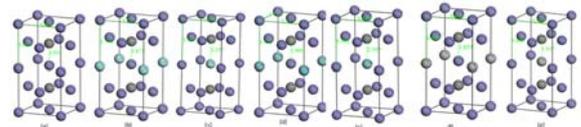


Fig. 2 Crystal structure optimization results of γ -Fe(C)-M

Figure 2 shows the structural optimization results of γ -Fe(C)-M model. It can be seen that whether Zr, Nb, V atoms displace Fe atoms at the top angle or the face centre in γ -Fe(C), they all increased the volume of the crystal cell to varying degrees and produced lattice distortion, indicating that all alloy atoms can strengthen γ -Fe(C) crystal cell. As shown in Figure 2(a), (c), (e) and (g), the crystal cell volume increased significantly when the alloy atoms displace the Fe atoms at face centre. This is mainly because the bond distances of Zr, Nb, V, and C are larger than those of Fe. The interatomic bonding force is weaker when the bond distance is larger. The bond distances of Zr, Nb, V and C atoms are 2.197 Å, 2.095 Å and 1.937 Å, respectively. Therefore, it can be concluded that V and C reaches its highest interatomic binding force. Nb reaches after it, and Zr is relatively weak. Compared with Figure 2(a), (b), (d) and (f), when the alloy atom displaces Fe atoms at the top angle in γ -Fe(C), the crystal cell volume changes little, and the bond distance between the alloy atom and Fe atom is less than that of C atom. This is mainly due to the fact that the radius of Zr, Nb and V differs from that of Fe atom by a small amount and from that of C atom by a large amount. The interatomic binding force between atoms is stronger if the crystal cell volume changes smaller, thus the crystal cell is more stable. It can be concluded from the above analysis that when the alloy atoms displace the Fe atoms at the top angle in γ -Fe(C), the volume of the crystal cell changes little, so Zr, Nb and V all priority to displace the Fe atoms at the top angle of the crystal cell in γ -Fe(C). Meanwhile, since the bond distance between V atom and Fe atom is the smallest (3.683 Å), crystal cell reaches its highest stability after V solid solution. Nb reaches after it, and Zr is relatively weak.

Table 1 Total cell energy of γ -Fe(C)-M

| | Total Energy (eV) |
|----------------------------------|-------------------|
| γ -Fe(C) | -7246.2.3084 |
| γ -Fe(C)-Zr (face centre) | -7661.9 |
| γ -Fe(C)-Zr (top angle) | -7663.4 |
| γ -Fe(C)-Nb (face centre) | -7932.3 |

| | |
|---------------------------------|---------|
| γ -Fe(C)-Nb (top angle) | -7933.3 |
| γ -Fe(C)-V (face centre) | -8357.4 |
| γ -Fe(C)-V (top angle) | -8358.1 |

Table 1 shows the total energy of γ -Fe(C)-M crystal cells. It can be seen that when Zr, Nb and V atoms displace the Fe atoms at the top angle, the total energy of the crystal cell is relatively low, indicating that crystal cell is more stable, and the alloy atoms are easier to be solid solution. This is completely consistent with the analysis results of structural optimization. When V atoms displace Fe atoms at the top angle in γ -Fe(C), the total energy of crystal cells is the lowest, followed by Nb and Zr is relatively weak. This also verifies the results of structural optimization from the perspective of total energy.

3.2. The results of Overlap charge distribution of γ -Fe(C)-M

Table 2 Overlap charge distribution of γ -Fe(C)-M

| bond | γ -Fe(C) | | γ -Fe(C)-Zr | | γ -Fe(C)-Nb | | γ -Fe(C)-V | |
|--------------|------------------------|---------|------------------------|---------|------------------------|---------|------------------------|---------|
| | Overlapping population | numbers |
| Fe-C | 0.31 | 4 | 0.84 | 4 | 0.34 | 2 | 0.32 | 2 |
| | 0.72 | 4 | 0.48 | 2 | 0.87 | 4 | 0.77 | 4 |
| | | | 0.29 | 2 | 0.44 | 2 | 0.34 | 2 |
| C-C | | | | | | | | |
| Fe-Fe | -0.33 | 8 | -0.40 | 4 | -0.07 | 4 | -0.27 | 4 |
| | 0.29 | 8 | 0.26 | 4 | -0.30 | 4 | 0.01 | 2 |
| | -0.03 | 2 | 0.16 | 2 | 0.31 | 4 | 0.85 | |
| | 0.82 | 2 | 0.84 | | 0.17 | 2 | -0.33 | 4 |
| | | -0.06 | 4 | 0.91 | | 0.29 | 4 | |
| M-C | | | | | | | | |
| Fe-M | | | 0.09 | | 0.06 | | 0.63 | |
| | | | -0.05 | 4 | -0.11 | 4 | 0.19 | 4 |
| Total | 8.08 | | 7.19 | | 7.58 | | 7.82 | |
| Anti-bonding | -2.70 | | -2.04 | | -1.48 | | -2.40 | |

It can be seen that the total overlapping population number of γ -Fe(C) is 8.08, which is basically consistent with the calculation results (8.12) in Ref. [18], indicating the accuracy of the calculation. In γ -Fe(C)-M crystal cell, part of Fe-M bond values are positive, indicating that there are electron clouds overlap between Zr, Nb, V atoms and Fe atoms, forming covalent bonds. The value of Fe-V bond overlapping population number is 0.63, which is the highest among Fe-M bonds, thus the covalent bonds between V and Fe atoms are the strongest. It is worth noting that the overlapping population number of Zr, Nb and Fe atoms are negative, indicating that Zr, Nb and Fe atoms are in an anti-bonding state and mutually exclusive. From the M-C bonds formed by Zr, Nb and V alloy atoms which are solid soluble in the γ -

Fe(C) crystal cell and the C atoms in the crystal cell, all the overlapping population numbers are 0. This indicates that in γ -Fe(C)-M crystal cell, there is no electron clouds overlap between Fe atoms and Zr, Nb, V atoms which are occupied to the top angle of the crystal cell in austenite. So it is difficult to form covalent bonds, only ionic bonds can be formed. This is completely consistent with the theory that Zr, Nb and V are strong carbide forming elements in alloy steel theory. From the perspective of total overlapping population numbers, the value of V is 7.82, which is higher than 7.58 of Nb and 7.19 of Zr. Therefore, to the bonding effect, γ -Fe(C)-V is the highest, followed by γ -Fe(C)-Nb and γ -Fe(C)-Zr is the weakest. It can also be explained on the other hand that the force between V atom and the atoms in the

austenite crystal cell is the highest, the crystal cell has the best stability, which is consistent with the analysis result of total energy. From the aspect of anti-bonding overlapping population numbers, the value of γ -Fe(C)-V is -2.40, which is the largest among the three. Thus, V atom will be strongly repelled by atoms in the crystal cell, and solid solution is relatively difficult. Therefore, compared with Zr and Nb, V is relatively difficult to be solid solution in γ -Fe(C) crystal cells, but once the solid solution is formed, the crystal cell will have the best stability.

The bonding effects of Zr, Nb, V alloy atoms with γ -Fe(C) crystal cells depends, on one hand, on the length of the bonds between the atoms, and on the other hand, on the participation of the atomic orbitals in bonding, which requires an analysis of the electronic structures.

3.3. Analysis of the differential charge density

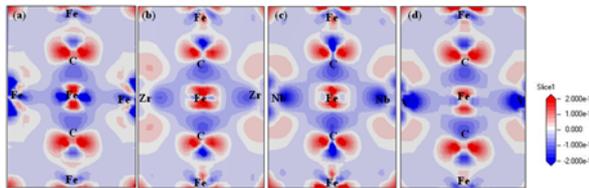


Fig. 3 differential charge density diagram of γ -Fe(C)-M crystal cell on the (110) plane

Figure 3 shows the differential charge density diagram of γ -Fe(C)-M crystal cell on the (110) plane. It can be seen that after solid solution replacements by alloy atoms, the density of electron cloud does not change much around C atom, while change obviously around Fe atom. The charge density of the central Fe atom in γ -Fe(C) crystal cell appears obvious directivity, showing the characteristics of covalent bond. The orientation of the charge density of the central Fe atom in the crystal cell is decreased to varying degrees by the alloy atoms replaced doping in by γ -Fe(C). The orientation of the charge density of the central Fe atom in γ -Fe(C)-V is the strongest, followed by γ -Fe(C)-Nb, and γ -Fe(C)-Zr is the weakest, indicating that the effect of the covalent bond is the most obvious in γ -Fe(C)-V and there are more metal bonds exist in γ -Fe(C)-Zr. On the other hand, the replaced doping of alloy atoms makes the charge density of the central Fe atom in the crystal cell lighter in color and less in covering area, indicating that the number of free electrons around the Fe atom decreased thus the number of electrons involved in bonding increased. The charge density of the central Fe atom in γ -Fe(C)-V is the lowest and it had the smallest coverage areas, thus, the number of the electrons around Fe atom involved in bonding is the most in γ -Fe(C)-V among γ -Fe(C)-M. Meanwhile, compared with Zr and Nb atoms, the density of electron cloud around V atom is the highest, which indicates that Fe-V bond has the strongest bonding effect.

3.4. Analysis of Binding energy of γ -Fe(C)-M

The mechanical properties and structural stability of alloy austenite are closely related to the binding energy of γ -Fe(C)-M crystal cells. The binding force among the

atoms is greater if the binding energy is higher, and it will require a higher energy to break the chemical bond of the atom. Thus, the crystal structure is more stable. The binding energy is calculated according to Equation 1.

$$E_0 = 1/n (E_n - E_{tot}) \quad (1)$$

Where, E_0 is the binding energy of the crystal cell, n is the number of atoms in the crystal cell, E_n is the total energy when the atoms in the crystal cell are in the free state, and E_{tot} is the total energy of the crystal cell (calculation results are shown in Table 1). In this paper, the free atoms energies of Fe, C, Zr, Nb and V are calculated, which are -860.58eV, -146.84eV, -1277.95eV, -1546.59eV and -1971.59eV, respectively. The atomic energy of Fe and C is basically consistent with the results calculated in Reg. [18] (-859.82eV, -145.88eV), indicating the accuracy of the calculation method in this paper. Combined with Table 1, the binding energy of γ -Fe(C)-M was calculated, the results are shown in Table 3.

| | E_0 /(eV/atom) |
|--------------------------------|------------------|
| γ -Fe(C) | 6.79 |
| γ -Fe(C)-Zr (top angle) | 6.71 |
| γ -Fe(C)-Nb (top angle) | 6.76 |
| γ -Fe(C)-V (top angle) | 6.90 |

It can be seen that the binding energy of crystal cells decreased after solid solution by Zr and Nb, indicating that both Zr and Nb atoms destroyed the stabilities of γ -Fe(C) crystal cell to some extent. After solid solution by V, the binding energy of crystal cell increased by 0.11eV, indicating that the solid solution of V atom increased the stability of crystal cell, which is significant to increase the stability of austenite. Therefore, it can be speculated that Zr and Nb atoms are likely to preferentially form carbides rather than solid solution in γ -Fe(C) crystal cell. This is consistent with the result in alloy steel theory that Zr and Nb are strong carbide forming elements, and the affinity of Zr and C is greater than that of Nb and V.

3.5. Discussion

The interaction between microalloying elements and austenite is an important basis for influencing the grain size of austenite, as well as one of the fundamental reasons for improving its mechanical properties. Meanwhile, the effect of alloying elements on the austenitizing of steel will directly affect the stability of the austenitic, which has important guiding significance for the heat treatment process. Although Zr, Nb and V are all strong carbide forming elements, their affinity to C atom is different. So there may be some differences in the microcosmic mechanism of Zr, Nb and V on microalloying of steel. First principle calculation shows that due to the differences in atomic radius and electronic structure of Zr, Nb and V, they have the same occupancy in γ -Fe(C) but obtained different binding energies in the

crystal cells. After solid solution by Zr and Nb, the binding energy of crystal cell is reduced, so Zr and Nb are more inclined to form ZrC and NbC strengthened phase with C atoms, which increases the hardness of the matrix itself. On the other hand, the strengthened phase can also hinder the growth of austenite grains, thus the grains are refined and the strength and hardness of materials can be improved. Therefore, Zr and Nb can mainly improve the mechanical properties of steel materials through dispersion strengthening. Zr and Nb shift the C curves to the left. It should be noted that the density functional method of the first principle calculations studied the low temperature ground state phases below room temperature, while austenite is the high temperature phase. There is no effective high temperature treatment method so far. After solid solution by V in γ -Fe(C), it affected the charge density of adjacent Fe atoms, enhanced the electron dispersion around Fe atoms, and had more electrons involved in bonding. It is the main factor for the increase of binding energy. In γ -Fe(C)-V, it has the most electrons involved in bonding. So after solid solution by V, the stability of austenite is the best. Therefore, V can shift the C curve to the right, which is of great significance to increase the hardenability of steel. It is worth noting that V does not change the charge density of adjacent C atoms very much, indicating that electrons around C atom do not participate much. The activity of C atom is not strong and inhibited by the Fe-V bond. Therefore, this is the main reason that the V element not only delays the transformation time of pearlite, but also changes the shape of austenite isothermal transformation, resulting in the double nose C curve.

4 Conclusions

In this paper, the total energy, binding characteristics, density of states, charge population and differential charge density of γ -Fe(C)-M cells formed by solid solution of Zr, Nb and V in γ -Fe(C) were calculated by using the first-principles method. Thus, the mechanism of Zr, Nb, and V with γ -Fe(C) was investigated. The main conclusions are as follows:

1) From the calculation results of the total energy of crystal cell, Zr, Nb and V all preferentially replaced the Fe atoms which are at the top angle in γ -Fe(C). Crystal cell reaches its highest stability after V solid solution. Nb reaches after it, and Zr is relatively weak.

2) From the calculation results of Overlap charge distribution, density electron of states and Mulliken charge population, in the γ -Fe(C)-Zr cell, Fe-Zr covalent bond and Zr-C ionic bond are the main chemical bonds. Fe3d, C2p and Zr4d orbitals are mainly involved in bonding. In γ -Fe(C)-Nb, Fe-Nb covalent bond is the main chemical bond with a number of Nb-C ionic bonds. Fe3d, C2p and Nb4d orbitals are mainly involved in bonding. In γ -Fe(C)-V, Fe-V covalent bond is the main chemical bond with a number of V-C ionic bonds. Fe3d, C2p and Nb4d orbitals are mainly involved in bonding. Compared with Zr and Nb, V is relatively difficult to be solid solution in γ -Fe(C) crystal cells, but once the solid

solution is formed, the crystal cell will have the best stability.

3) From the calculation results of differential charge density, the electron cloud density around C atom changed little, while Fe atom changed obviously. The orbital electrons around Fe atoms in γ -Fe(C)-V has maximal distribution, which means that the electrons delocalized most and most of the electrons are bonding. It is the main factor for the increase in the binding energy of crystal cell.

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