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THE POINT DEFECTS OCCUPANCY RULE OF V ATOMS INTO Ni_3Al ALLOY

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Abstract. By using the first-principles, electronic structure and point defects occupancy rule of Ni_3Al alloy were studied. The approximate computation method of Ni_3Al alloy was selected by comparing experimental results with the computation. The lattice constant, the formation enthalpy, cohesive energy and density of states of the supercell were computed. The results showed that: anti-site defect formation enthalpies were less than vacancy defects in Ni_3Al alloy, NiAl was the most important anti-site defects in Ni_3Al alloy. The alloy phase formed by V atoms into Ni_3Al alloy system could play a role of strengthen, the Al sites were the most likely formation of defects in the Ni_3Al alloy.

1. INTRODUCTION

The Ni_3Al intermetallic compound has the advantages of high stability, low density, high rate of work-hardening at room temperature and strongly high temperature oxidation resistance. The application prospects in the high-temperature structural materials are very broad [1-2]. However, a single Ni-Al alloy at high temperature has low strength, poor corrosion resistance and production brittle phase easy at low temperatures. In order to improving toughness of Ni-Al alloy at low temperature and enhancing the strength, oxidation and corrosion resistance at high temperature, people often add Cr, V, Al, Ti, Zr, Mg, and rare earth elements into Ni_3Al to form a series of Ni-Al high temperature alloy.

The crystal point defects play an important role in the physical properties of intermetallic compounds. Many crystal physical and mechanical properties greatly relate to the presence of point defects. Therefore, the study of crystal point defects have an important significance in understanding the material properties of micro and macro. The current Ni_3Al point defects are mostly studied by means of computer. The methods mainly contain first-principles, ab initio method, embedded atom method (EAM) and microscopic phase field method *et al.* The software used mostly contain Material studio, VASP *et al.* The ease of formation defects is characterized by calculating the intermetallic compounds formation enthalpies. CL FUt *et al.* studied Ni_3Al point defects by first-principles. The results showed that the vacancy formation enthalpies can be significantly larger than the anti-sites. The Al sites vacancy formation enthalpies were greater than Ni sites. The Ni anti-site formation enthalpy was greater than Al sites. The Ni_3Al anti-site defects can be easily formed than the vacancies. In different atomic locations point defects formed in different degrees of difficulty [3].Song Yu *et al*. studied Ni_3Al point defects by EAM, and found that there were anti-site defects in Ni_3Al alloy [4]. Hannes *et al.* calculated the Ni_3Al formation of point defects by ab initio method, the same found that vacancy formation enthalpies were significantly larger than the anti-sites. The results calculated in different approximate methods likely had some differences [5]. C. Jiang *et al.* studied the Ni_3Al point defects by

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first-principles, found that point defects occupancy rule affected by the temperature [6]. Zhang *et al.* studied anti-site defects in Ni_3Al of $Ni_{75}Al_xV_{25-x}$ by microscopic phase field method, found that Ni_3Al anti-site defects contained Al_{Ni} ,V_{Ni} ,Ni_{Al}, V_{Al} and the concentration of anti-site defects effected by Al [7]. All of these approaches studied Ni_3Al point defects from different perspectives and reached the same conclusion: the Ni_3Al anti-site defects were easier to form than vacancies, but their study had a different focus, this article would have further research in their study.

Cambridge serial total energy package (CASTEP) can effectively researches point defects and electronic structure in metal material, which own strong visualization capability and easy operation. This paper calculated V atoms into Ni_3Al alloy point defects by castep , which included four kinds of anti-site defects Al_{Ni}, V_{Ni}, Ni_{Al}, V_{Al} and two kinds of vacancy defects Ni_{vac}, Al_{vac}. We analyzed the vacancy and anti-site formation enthalpies firstly, and then considered different anti-site formation enthalpies, analyzed the occupancy rule by comparing the formation enthalpies and studied the Ni_3Al electronic structure and analyzed bonding capacity. Above all it have reached the purpose of explaining the Ni_3Al alloys macro properties from the point of micro, which provided a theoretical reference for further study in the Ni-Al-V alloy.

2. BASIC OF THEORY

In dealing with multi-electron kinetic energy about density functional, Kohn-Sham put interaction term into the exchange-correlation potential $Exc[\rho(r)]$, changed the complex multi-electron problem into single-electron problem [8]. so multi-electron system can be described by the single-electron K-S equation. The exchange-correlation items E_{XC} $[\rho(r)]$ in K-S equation used the variational method to solve self-consistent and thus obtained the basic properties of solid materials, but the functional form of E_{XC} $[\rho(r)]$ for $\rho(r)$ was unknown. At present the various total energy computation methods based on first-principles had adopted the local density approximation [9] (LDA). Dealing with exchange-correlation potential in the form of:

$$V_{XC} = \frac{\delta E_{XC}\left[\rho(r)\right]}{\sigma\rho(r)}, \tag{1}$$

where E_{XC} is the exchange-correlation energy, $\rho(r)$ is the electron density.

In the computing system of molecule and a small cluster, LDA often gives bond energy values much larger than the experimental value [10]. The reason lattice constant (bond length) compared with the experimental value too small was that LDA ignored inhomogeneous electron gas near to r sites which effected single-electron exchange-correlation energy, the same ignored the impact of the electron density gradient. The generalized gradient approximation (GGA) [11] took the changes in electron density into account, at this time the exchange-correlation potential was:'

$$V_{xc} = \frac{\delta E_{xc}\left[\rho(r)\right]}{\delta\rho(r)} = \frac{\partial\left[\rho(r)\varepsilon_{xc}(r)\right]}{\partial\rho(r)} - \nabla\frac{\partial\left[\rho(r)\varepsilon_{xc}(r)\right]}{\partial\rho(r)}. \tag{2}$$

Relative to the LDA, GGA can gave a more accurate bond energy value and easily integrates into the algorithm of LDA.GGA had been widely used for a variety of computing software based on density functional theory (DFT).Exchange-correlation potential based on LDA and GGA had many different forms, such as the the Kohn-Sham-Gaspar exchange potential [12], Slater an average exchange potential [13], Slter-X^{α} exchange potential [14], Wigner correlation energy, Ceperley-Alder exchange-correlation potential *et al.* based on LDA. The exchange-correlation potential based on GGA have PW91 [15], RPBE and PBE [16] *et al.* All-electronic potential was the atomic sphere approximation based on the Muffin-Tin ball, which selected the centro-symmetric potential in ball and took their constant potential in the gap, then followed the method of plane wave to start and uses the variational principle for solving KS equation, obtained the self-consistent solution of the problem. This paper would make two kinds of approximation compared with the experimental results for determining approximate method that suitable for this computation system.

3. MODELS OF COMPUTATION

Ni_3Al alloy has an ordered face-centered cubic and the $L1_2$-type ordered derivative structure. Ni atoms occupy the six face-centered 3c location in cell, Al atoms occupy the eight corners 1a location in cell, its atomic space layouts show in Fig. 1. Lattice constant: a_0 = 0.3589 nm, $\alpha = \beta = \gamma = 90°$.Space group is PM-3M.

Ni_6Al_2 (1x1x2) supercell (8 atoms) was used in the computation. Two kinds of vacancy defects Ni_{vac}, Al_{vac} and four kinds of anti-site defects Al_{Ni}, V_{Ni}, Ni_{Al}, V_{Al} were constructed. Occupancy rule was showed by comparing the formation enthalpy with binding

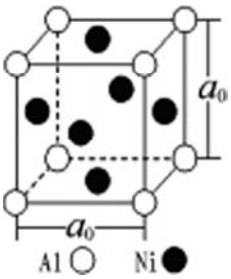

Fig. 1. Structure of Ni_3Al.

energy. Also the density of states was analyzed for performance of structural stability. The specific supercell structures as shown in Fig. 2.

4. METHOD OF COMPUTATION

CASTEP was the first-principles plane-wave pseudopotential method based on the density functional theory, the crystal wave functions launched by Plane Wavelet Group using periodic boundary conditions, in which the exchange-correlation potential adopted GGA- PW91and LDA-CA-PZ. A plane wave cutoff energy 459.9 eV was used in GGA, other plane wave cutoff energy 270 eV was used in LDA. Before the computations, Broyden-Flecher-Goldfarb-Shanno (BFGS) method was adopt in a variety of supercell model geometry optimized in order to achieving the most stable structure in their local area. Pulay density hybrid method was applied in the self-consistent computation (SCF). Self-consistent convergence condition setting: the total energy was less than 0.2×10^{-4} eV atom, the force in each atom was less than 0.05 eV /Å, the offset tolerance was less than 0.002 Å and the Stress bias was less than 0.1 GPa.

Ni_3Al cell geometric structure optimization taken by LDA, GGA and the corresponding parameters ,and calculated its properties as shown in Table 1. A suitable approximation was choosn by equilibrium lattice constants, formation enthalpies and cohesive energies compared with the experimental values and other computation results.

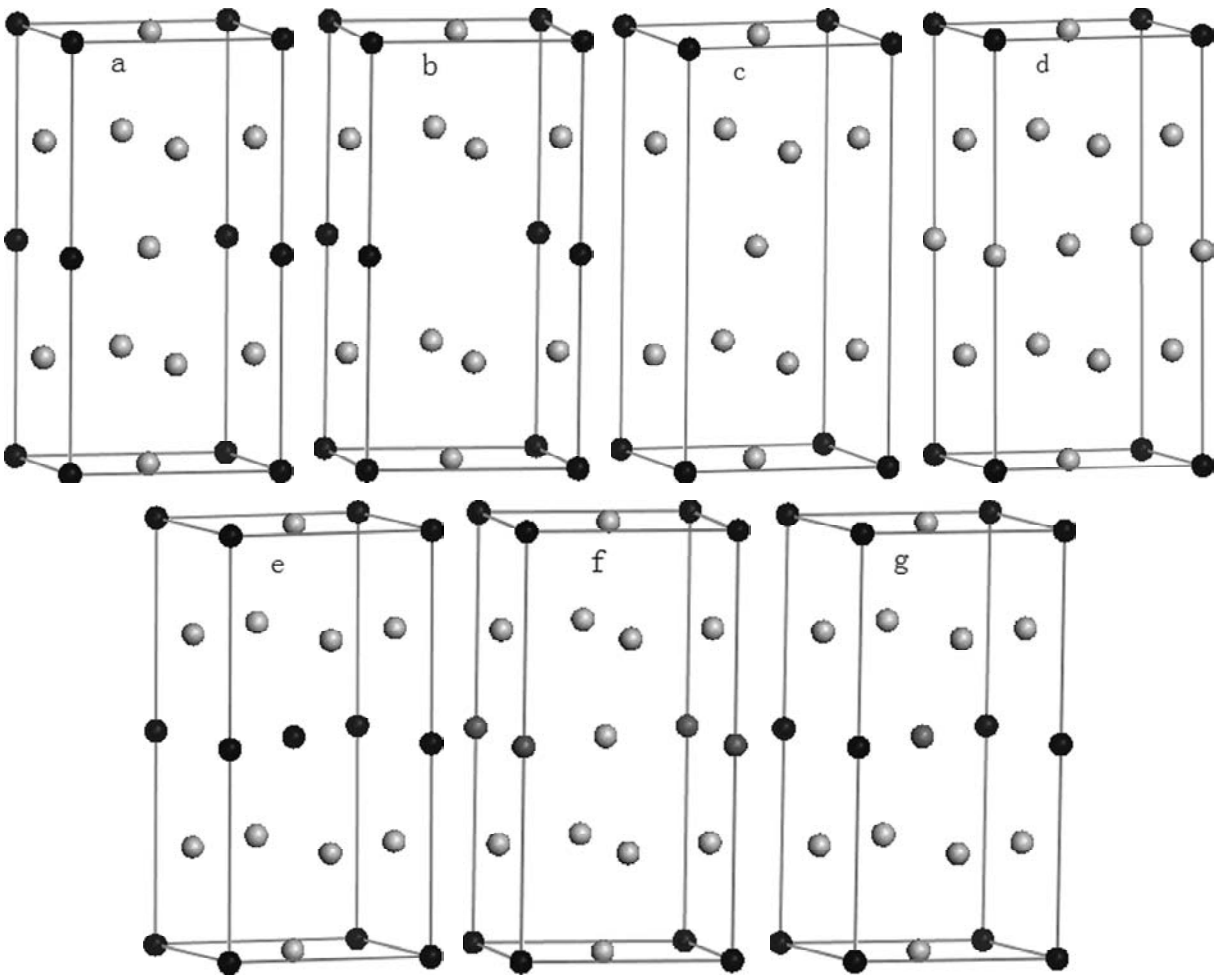

Fig. 2. (a) represent idea supercell Ni_6Al_2; (b) represent $Ni_5Al_2(Ni_{vac})$; (c) represent $Ni_6Al\ (Al_{vac})$, (d) represent $Ni_7Al\ (Ni_{Al})$, (e) represent $Ni_5Al_3\ (Al_{Ni})$, (f) represent $Ni_6AlV(V_{Al})$, (g) represent $Ni_5Al_2V(V_{Ni})$.

Table 1. Properties of Ni_3Al.

	Parameter, *a*/nm	formation enthalpy, eV/atom	cohesive energy, eV/atom
LDA	0.3528	-0.5907	-4.5753
GGA	0.3574	-0.5025	-3.6517
calculation	0.3572 [17]	-0.4486 [18]	
experiment	0.3563[17]		

Table 2. Lattice parameter of the supercell.

Formula	*a*/nm	*b*/nm	*c*/nm	*V*/nm^3
Ni_6Al_2	0.35797	0.35798	0.71305	0.0913748
$Ni_5Al_2(Ni_{vac})$	0.35450	0.35450	0.69695	0.0875867
$Ni_6Al\,(Al_{vac})$	0.36102	0.36101	0.65107	0.0848577
$Ni_7Al\,(Ni_{Al})$	0.35472	0.35472	0.71152	0.0895304
$Ni_5Al_3\,(Al_{Ni})$	0.38326	0.38326	0.64365	0.0945452
$Ni_6AlV(V_{Al})$	0.35740	0.35741	0.71105	0.0908323
$Ni_5Al_2V(V_{Ni})$	0.36886	0.36887	0.69869	0.0950677

It can be seen from Table 1, the lattice constant a and the formation enthalpy calculated by GGA were closer to the calculated or experimental values of others than LDA, so GGA was more appropriate for studying Ni_3Al anti-site defects, GGA will be taken to the following computations.]

5. COMPUTATION RESULTS AND DISCUSSION

5.1. Lattice constant

The supercell balance lattice constants listed in Table 2. As the three types of atomic radius with the following relationship: $r_{Al}>r_V>r_{Ni}$, when there were defects such as $V_{Al,}$ Ni_{vac}, Al_{vac}, and Ni_{Al}, it would result in lattice distortion, lattice constant reduction and cell contraction; When there were Al_{Ni} and V_{Al} two kinds of defects, it would make lattice constant raising and cell swelling; Supercell $Ni_6AlV(V_{Al})$ and $Ni_5Al_2V(V_{Ni})$ maintained the same crystal structure with Ni_6Al_2, lattice constant changed little.

5.2. The total energy of supercell and the bonding electrons under the Fermi level

5.2.1. The total energy of supercell

In the cases of other parameters unchanged and the same supercell structure, the total energy of supercell was the lower and the more stable. We can see from Table 3. The total energy of the following supercell incremental and stability reduction, $Ni_6AlV(V_{Al}) < Ni_7Al(Ni_{Al}) < Ni_5Al_2V(V_{Ni}) < Ni_6Al_2 < Ni_6Al(Al_{vac}) < Ni_5Al_3(Al_{Ni}) < Ni_5Al_2(Ni_{vac})$. The total energy of $Ni_6AlV(V_{Al})$ was the lowest and the state was the most stable, it showed that V atoms into Ni_6Al_2 can significantly increased the Ni_6Al_2 strength and enhanced the stability of Ni-Al alloy.

5.2.2. The bonding electrons under the Fermi level

The bonding electrons under Fermi level can reflect the stability of supercell the different components and the same structure. The supercell interaction and structure stable were the strong when the number of bonding electrons was big. It can be seen from Table 3, the bonding electrons of the following supercell feebler and stability reduction, $Ni_6AlV(V_{Al})> Ni_7Al(Ni_{Al}) >Ni_5Al_2V(V_{Ni}) > Ni_6Al_2> Ni_6Al(Al_{vac})> Ni_5Al_3(Al_{Ni})> Ni_5Al_2(Ni_{vac})$, the same conclusion about computation supercell total energy was drawn.

5.3. The formation enthalpy and cohesive energy

5.3.1. The formation enthalpy

The formation enthalpy is energy can be released or absorbed after the reaction to a substance. The formation enthalpy of exothermic reaction is negative, which is that the total energy of resultants is less than the total energy of the reactants. The formation enthalpy of endothermic reaction is positive, which is that the total energy of resultants is greater than the total energy of the reactants. It

Table 3. Properties of the supercell.

Formula	Total energy/eV	Formulation enthalpy /eV·atom^{-1}	Cohesive energy/eV·atom^{-1}	Number of Electrons below Fermi energy/Electrons
Ni_6Al_2	-8257.3535	-0.4992	-3.6489	66
$Ni_5Al_2(Ni_{vac})$	-6898.8066	-0.3124	-3.3815	56
$Ni_6Al\ (Al_{vac})$	-8197.4677	-0.08109	-3.4728	63
$Ni_7Al\ (Ni_{Al})$	-9555.6826	-0.5983	-3.6873	73
$Ni_5Al_3\ (Al_{Ni})$	-6957.8548	-0.5968	-3.4645	59
$Ni_6AlV(V_{Al})$	-10177.8698	-0.4375	-3.9972	76
$Ni_5Al_2V(V_{Ni})$	-8877.4899	-0.4249	-3.7025	69

can be used to indicate the degree of difficulty in the formation of intermetallic compounds. When the formation enthalpy is negative, the greater its absolute value, it indicates that the more easy formation of intermetallic compounds. The formation enthalpy formula [19] is as follows:

$$E_{form} = \frac{1}{x+y+z}\left(E_{tot} - xE_{solid}^{Ni} - yE_{solid}^{Al} - zE_{solid}^{V}\right), \quad (3)$$

where E_{tot} is total energy of supercell. E_{solid}^{Ni}, E_{solid}^{Al}, E_{solid}^{V}, respectively, represent the average energy of each atom ,which are solid fcc-Ni, fcc-Al, and bcc-V atom. *x*, *y*, and *z* respectively represent the atom number in the supercell structure model, which are Ni, Al and V atom. When calculating the energy of solid-state single-atomic, the same computation conditions should be taken to the total energy of intermetallic compound supercell.

The computation results in Table 3 can be seen that the formation enthalpy of each supercell were negative. It indicated that they could form stable structure. The absolute value of the following supercell formation enthalpy feebler and the difficulty of formation increasing:$Ni_7Al\ (Ni_{Al})$ > $Ni_5Al_3\ (Al_{Ni})$ > Ni_6Al_2 > $Ni_6AlV(V_{Al})$ > $Ni_5Al_2V(V_{Ni})$ > $Ni_5Al_2\ (Ni_{vac})$ > $Ni_6Al(Al_{vac})$. It showed that the formation enthalpy of vacancy defects $Ni_5Al_2(Ni_{vac})$ and $Ni_6Al\ (Al_{vac})$ were larger than the anti-site defects, which proved the formation of vacancy defects were more difficult that anti-sites. This was consistent with the computation results of Hannes schweiger [5] *et al.* The absolute value of the $Ni_7Al\ (Ni_{Al})$ formation enthalpy was the largest and it's more easy to form a stable compound. Therefore it has a strong alloying ability and is the most significant anti-site defect in Ni_3Al alloy; The absolute value of the $Ni_6AlV(V_{Al})$ formation enthalpy was larger than $Ni_5Al_2V(V_{Ni})$, which proved V in the Ni_3Al structure were preferable to the Al sites. This was consistent with the computation results of Zhang Jing [7] *et al.* Based on comparing the Ni site defects formation enthalpy with Al sites defects in Ni_3Al alloy, it showed that Al sites in Ni_3Al alloys were more easy to form defects.

5.3.2. Cohesive energy

Cohesive energy is closely related to crystal strength and structural stability. Crystal cohesive energy is the energy released by free atoms combined to crystal, the same is the energy made by the outside world power when crystal broken down into single atoms. The greater the absolute value of cohesive energy, the more the formation of crystals stable [20]. Cohesive energy formula is as follows:

$$E_{coh} = \frac{1}{x+y+z}\left(E_{tot} - xE_{atom}^{Ni} - yE_{atom}^{Al} - zE_{atom}^{V}\right), \quad (4)$$

where E_{tot} also is total energy of supercell, E^{Ni}_{atom}, E^{Al}_{atom}, $E^{V}_{atom,}$ respectively, represent the free atoms energy ,which are Ni, Al, V atom. *x*, *y*, and *z* respectively represent the atom number of in the supercell structure model, which are Ni, Al, and V atom. When calculating the energy of free atoms, the same computation conditions should be taken to computing the intermetallic compound supercell total energy.

From Table 3, the computation results can be seen, the cohesive energies of each supercell were negative. It indicated that they can form stable structure. The absolute value of the following supercell cohesive energy feebler and the stability reduction: $Ni_6AlV\ (V_{Al})$ > $Ni_5Al_2V(V_{Ni})$ > $Ni_7Al\ (Ni_{Al})$ > Ni_6Al_2 > $Ni_6Al\ (Al_{vac})$ > $Ni_5Al_3\ (Al_{Ni})$ > $Ni_5Al_2(Ni_{vac})$, $Ni_6AlV(V_{Al})$ formed by V atoms into Ni_3Al alloy ,it's the absolute value of cohesive energy was the largest ,and it was the most stable. The absolute value of $Ni_5Al_2V(V_{Ni})$ cohesive energy was the second large, and it was also stable. It indicated that V acces-

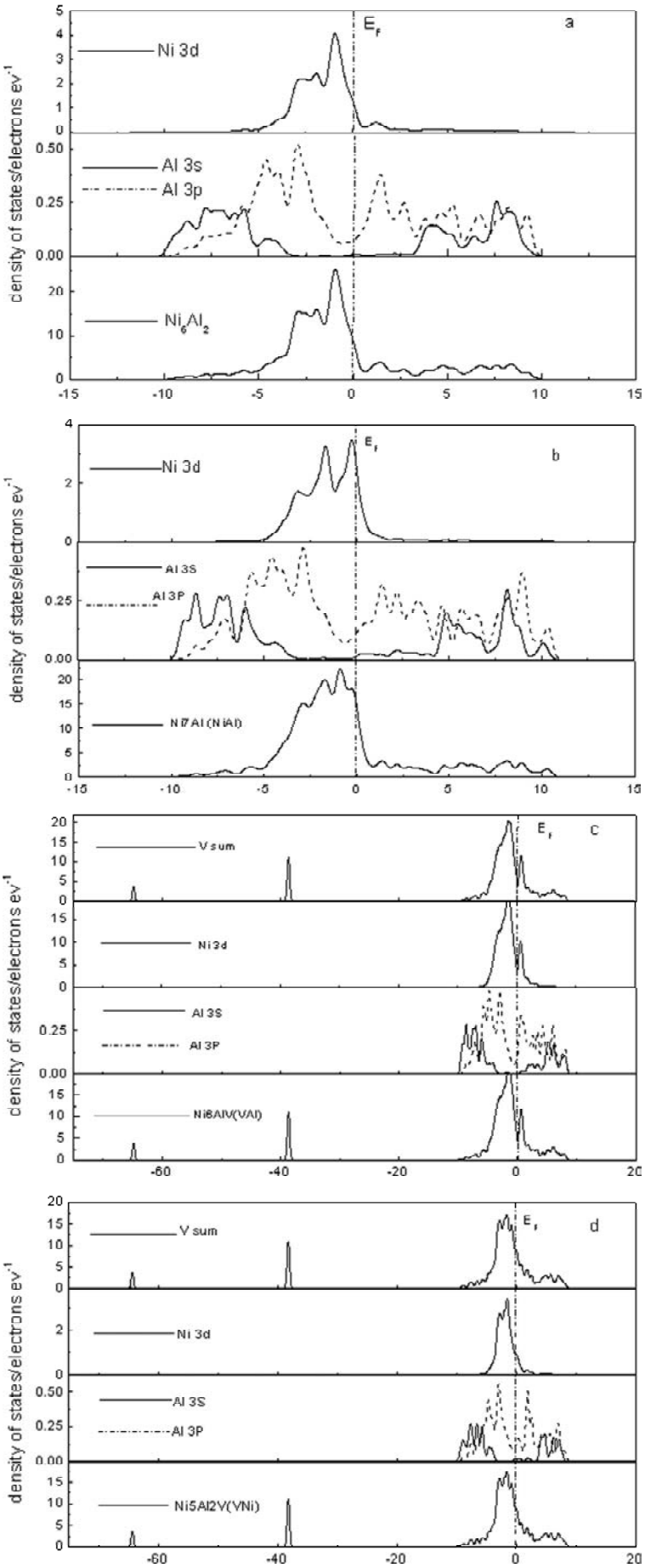

Fig. 3. DOS of the representative supercell: (a) Ni_6Al_2; (b) $Ni_7Al(Ni_{Al})$; (c) $Ni_6AlV(V_{Al})$; (d) $Ni_5Al_2V(V_{Ni})$.

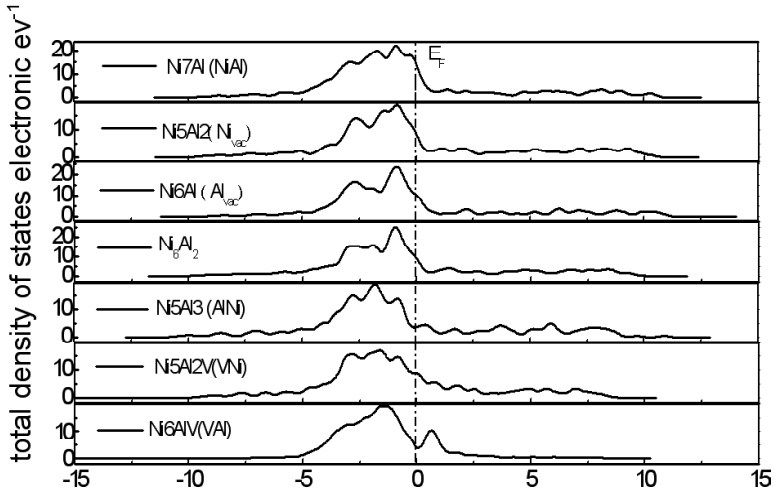

Fig. 4. The total density of state the all supercell.

sion can improve the Ni_3Al alloy strength and play the role of strengthening effect. The stability of Ni_5Al_2 (Ni_{vac}) was the worst and Ni_6Al (Al_{vac}) was the second bad. it showed that Ni_3Al vacancy defects can not be stable but anti-site defects were the main defects.

5.4. Density of state

Selecting several representative supercell for density of states computation, As shown in Fig. 3. Ni valence electrons were 3d8 $4s^2$, Al valence electrons were $3s^2$ 3p1,V valence electrons were $3s^2$ 3p6 3d3 $4s^2$. The bonding electron of Ni_6Al_2 mainly distributed in–10~10 eV, it mainly contributed by valence electron of Ni3d and Al3s, 3p; The distribution of the Ni_7Al (Ni_{Al}) and Ni_6Al_2 valence electron were the basically same, but density of states above the Fermi level vary widely, Ni_7Al (Ni_{Al}) density of states was very high. According to the smaller density of states at E_F, the more stable system, it can be seen Ni_6Al_2 was more stability than Ni_7Al (Ni_{Al}), which were consistent with the conclusions of the previous computations; The $Ni_6AlV(V_{Al})$ bonding electron mainly distributed in the -66 ~-64 eV, -39 ~-37 eV and -9 ~ 8.5 eV, the bonding electron in -39 ~-37 eV mainly contributed by V valence electron, in -9 ~ 8.5 eV mainly contributed by the Ni3d and V valence electron. In comparison, $Ni_6AlV(V_{Al})$ there were two strong bonding peaks under the Fermi lower level, occupied a wide level–66~8.5 eV while Ni_6Al_2 occupied a narrow level -10~10 eV, which further proved that the stability of $Ni_6AlV(V_{Al})$ beyond of Ni_6Al_2. $Ni_5Al_2V(V_{Ni})$ in -65 ~-63 eV, -39 ~-37 eV range the major contributed by the V valence electrons. In the context of -10 ~ 8.5 eV mainly contributed by the valence electron of Ni_3d, Al3s, 3p, and V. Above all, V atoms into Ni-Al alloy will lead to $Ni_{75}Al_xV_{25-x}$ bonding electrons under the Fermi energy lower level increase and stability enhance, the same was the strength of Ni-Al-V alloy higher than Ni - Al alloy.

Conducting density of states computations, the relationship between the density of states and stability of the system generally believed system was stable when E_F was close to the energy gap or the pseudo-band gap bottom. In Fig. 4 showed the total density of states all supercell, from which we can found the Ni_6AlV (V_{Al}) total density of states value at E_F lay at the bottom of the energy gap, therefore $Ni_6AlV(V_{Al})$ was the most stable. It was consistent with the conclusions of above study, and proved the previous conclusions in other point of view.

6. CONCLUSIONS

Using the first-principles, electronic structure and point defects occupancy law of Ni_3Al alloy were studied and found:

1) GGA is more appropriate than the LDA in Ni_3Al alloy point defect study;

2) V give priority to replacement Al-sites in the Ni_3Al alloy. The formation of new phase and parent phase maintain the same crystal structure, lattice constant change little;

3) Al-sites easily form defects in Ni_3Al alloy, $Ni_6AlV(V_{Al})$ is the most stable alloy phase, V atoms into Ni_3Al alloy can play a role of strengthening effect;

4) The formation of vacancy defects are more difficult than the anti-site defects in Ni_3Al alloy, Ni_7Al (Ni_{Al}) is the most easy to form and stable alloy phase, Ni_{Al} is the most important anti-site defects.

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