First-principles calculations of magnetic and mechanical properties of Fe-based nanocrystalline alloy Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$

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Abstract

Based on the first-principles calculation method of density functional theory (DFT), the crystal structure, band structure, magnetic moment, density of state, elastic constant and population analysis of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ are calculated. The calculation results show that the Fe-based nanocrystalline alloy of this composition has a stable structure, strong resistance to deformation, high hardness and is an alloy with good flexibility. The energy band structure of spin-up and spin-down is basically the same, and the energy gap is 0 eV, showing metallicity. The asymmetry of the electronic state density between the spin-up and spin-down states indicates that the alloy is ferromagnetic, with a magnetic moment of 84.15 $\mu_B$; the Fe element plays a decisive role in the magnetic properties of this alloy.

Keywords: first principles, Fe-based alloy, magnetic properties, elastic constant

1 Introduction

Electrical equipment such as current transformers, voltage transformers and transformers in power systems require core materials with magnetic properties that meet the corresponding requirements. For example, for current transformers, the accuracy is relatively high only when the measured current is near the rated current. When the measured current is much smaller or much larger than the rated current, it is limited by the initial permeability and saturation magnetic induction of the core material, and the measurement accuracy becomes greatly reduced. Therefore, for extending the measurement range of the current transformer, an important way is by improving the magnetic properties of the core material. In addition, for current transformers, the mechanical properties of the core material are often considered in various application conditions.

There are many literatures on the composition and magnetic properties of the core materials [1–5]. Gubanov et al. [6] found that the band structure of electrons is mainly determined by the short-range order structure of atoms, and therefore believed that iron-based nanocrystalline alloys are ferromagnetic. Duwez et al. [7] prepared
an Fe$_{80}$P$_{12.5}$C$_{7.5}$ amorphous alloy using the alloy solution quenching method, and carried out the magnetic test, which proved that the iron-based amorphous alloy is magnetic. Japan’s Hitachi Metals Company Yoshizawa Kren doped Nb or Cu into Fe-Si-B, and processed the alloy solution to obtain Fe-Si-B-Nb-Cu nanocrystalline alloy [8]. Its main component is Fe$_{73.5}$Cu$_{1}$N$_{3}$Si$_{13.5}$B$_{9}$. Suzuki et al. [9] experimentally prepared Fe-N-B (N=Zr, Nb, Hf, etc.) nanocrystalline alloys with high saturation magnetic flux density and low coercivity, the main component of which is Fe$_{90}$Zr$_{7}$B$_{3}$. The 1K107 Fe-based nanocrystalline alloy is an alloy formed by doping the Fe element as the main element and then doping an amount of Si, Nb, B and Cu elements. It is a soft magnetic material, having many advantages such as low loss, low coercivity and high saturation magnetic induction, and is widely used in current transformer cores and other power equipment [10, 11]. At present, most researches on Fe-based nanocrystalline alloys are based on experiments, and there are relatively few studies on Fe-based nanocrystalline alloys in theory. Therefore, this paper uses the first-principles calculation method based on density functional theory (DFT) [12] to calculate and analyse the band structure, density of state, magnetic properties and elastic constants of Fe$_{80}$Si$_{10}$Nb$_{6}$B$_{2}$Cu$_{2}$. The research results of this paper can be used as the basis for the selection of iron core materials of electrical equipment such as current transformers.

2 Structural model and calculation method

2.1 Structural model

Figure 1 shows the structure model of the Fe-based nanocrystalline alloy Fe$_{80}$Si$_{10}$Nb$_{6}$B$_{2}$Cu$_{2}$, with its lattice constant $a=5.7328$, $b=c=14.332$, and the crystal face angle $\alpha = \beta = \gamma = 90^\circ$. It is a 1K107 material with different element ratios. This paper establishes a $2 \times 5 \times 5$ Fe supercrystal cells, a total of 100 Fe atoms, and then randomly replaced Fe atoms with 10 Si atoms, 6 Nb atoms, 2 B atoms and 2 Cu atoms, respectively, thereby establishing the Fe$_{80}$Si$_{10}$Nb$_{6}$B$_{2}$Cu$_{2}$ model.

![Fig. 1 The model of Fe-based nanocrystalline alloy Fe$_{80}$Si$_{10}$Nb$_{6}$B$_{2}$Cu$_{2}$.](image)

2.2 Calculation method

The calculation in this paper is carried out by the Cambridge sequential total energy package (CASTEP) [14] software package based on the plane wave geese potential method. For ensuring the reliability and stability of the calculation, and to obtain a crystal model close to the actual structure, we first use DFT to process the
interaction between ions and electrons, and use generalised gradient approximation (GGA) PBE [13] basis set which deals with the exchange correlation energy between atoms and then optimise the geometric structure of the Fe-based nano-alloy to obtain a stable crystal structure. Finally, the density of states, energy band structure, elastic constants, magnetic properties and population analysis are calculated and analysed for the stable crystal structure.

In this paper, the cut-off energy of the plane wave is set to 330 eV, select 3 × 3 × 1 for k-point sampling, and set the spin polarisation conditions to calculate and analyse the spin-down and spin-up electrons in the Fe80Si10Nb6B2Cu2 crystal. In the iterative process, the single-atom energy convergence accuracy is 2 × 10−5 eV/atom, the maximum stress is 0.10 GPa and the convergence standard for the maximum displacement between atoms is 0.002 Å. In this calculation, the valence electron of each atom is Fe-3d64s2, Si-3s23p2, Nb-4d45s1, B-2s2p1 and Cu-3d10.4s1.

3 Analysis of calculation results

3.1 Density of states and band structure

Figure 2 shows the spin-up and spin-down band structures of this material. One of the sources of electronic magnetism is the magnetic moment produced by the electron spin. The spin is closely related to the material’s magnetic properties, so the spin-up and spin-down band structures are calculated. The Fe-based nanocrystalline alloy Fe80Si10Nb6B2Cu2 has a total of 786 electrons near the Fermi level (energy is zero), of which there are 565 spin-up electrons and 221 spin-down electrons. After optimising the structure of Fe80Si10Nb6B2Cu2, the energy band structure is calculated. This paper mainly intercepts the energy band range of −10−110 eV. It can be seen in Figure 2 that the spin-up and spin-down energy band structure diagrams of Fe80Si10Nb6B2Cu2, Figure 2 shows that the Fermi energy level passes through the energy band in both the spin-up and spin-down directions, and the energy gap is 0, showing metallic properties.

In addition, it can be seen from Figure 2 that the spin-up and spin-down band structure dispersion of Fe80Si10Nb6B2Cu2 is significantly different, indicating that the alloy has spin splitting. Therefore, this shows that Fe80Si10Nb6B2Cu2 has strong magnetic properties. Near the Brillouin zone Q, the energy band is very gentle, so the effective mass m of carriers will be relatively large, resulting in a relatively large Seebeck coefficient S of the alloy system.

Figure 3 shows the total density of states of Fe80Si10Nb6B2Cu2 near the Fermi level and the partial density of states of each atom. This paper mainly intercepts the density of states diagram with energy from −15 eV to 25 eV. It can be seen from the figure that the density of states of Fe80Si10Nb6B2Cu2 is mainly composed of Fe-4s, Si-3p, Nb-4d, B-2P state and Cu-3d state. In the low-energy region with energies ranging from −15 eV to 0 eV, that is, at the left side of the Fermi level, the density of states is mainly composed of Fe-4s state, Si-3s state, Nb-4d state, B-2s state and Cu-3d state. On the right side of the Fermi level, the density of states is mainly composed of Fe-3p, Si-3p, B-2P and Nb-4p state. And there are two obvious peaks near the Fermi level, and the distance between the two peaks is called the pseudo-energy gap. The wider the pseudo-energy gap, the stronger the ability to form bonds between atoms and the stronger the covalent nature of the substance. Therefore, this pseudo-energy gap is mainly provided by the localised Fe-3d electron orbital of the transition metal, in which the density of each partial wave state crosses the Fermi level, showing obvious metallic properties.

When the energy is −13.41 eV, the Si atom has a peak, which is mainly composed of electrons in the Si-3s orbital. Here, there is also a tiny peak of Fe-3d orbital, which overlaps with the peak of Si-3s orbital. It can be explained that there is a charge transfer between Si-3S and Fe-3d orbital, and then a chemical bond is formed. The typical population numbers and magnetic moments of bonds between several adjacent atoms are shown in Table 1.

Table 1 shows that the magnetic moment of the chemical bond formed between adjacent atoms is very small, close to 0, indicating that the alloy has a full-shell structure due to the transfer of electrons.
Fig. 2 Band structure of Fe-based nano-alloys Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$.

Fig. 3 The DOS and PDOS of Fe-based nano-alloys Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$. 
Table 1 Population and magnetic moment of bonding between adjacent elements.

| Bond   | Population | Spin(µB) |
|--------|------------|----------|
| Fe-Fe  | 0.15       | 0.02     |
| Fe-Si  | 0.35       | 0.01     |
| Fe-Nb  | −0.01      | −0.01    |
| Fe-B   | 0.16       | 0.01     |
| Fe-Cu  | −0.17      | 0.05     |
| Si-B   | 0.17       | −0.00    |
| Si-Cu  | 0.34       | −0.00    |
| Nb-B   | −0.11      | −0.01    |
| Nb-Cu  | −0.25      | −0.00    |
| B-Cu   | 0.28       | 0.01     |
| Si-Si  | 0.22       | −0.00    |
| Nb-Nb  | −0.42      | 0.14     |

3.2 Magnetic performance analysis

Figure 4 is the electron spin state density diagram of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$. According to quantum mechanics, spin is a basic characteristic of electrons. After the magnetised ferromagnetic material, the electrons will generate two kinds of carriers with spin-up and spin-down [14]. It can be seen from the figure that the spin up and down density of states of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ near the Fermi level is not symmetrical, and the difference is very large. In both the spin up and down state densities, the peak of the state density appeared near $-1.77$ eV, resulting in the phenomenon of spin splitting, indicating that the alloy is magnetic.

![Fig. 4 Spin density of states of Fe-based nano-alloys Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$.](image)

There is a large peak near the Fermi level; Figure 5 shows that this is mainly caused by the hybridisation of the 4s of Fe atoms and the 4d electron orbitals of Nb atoms, and Fe atoms in particular play most of the role. It can be seen from the figure that the upper and lower spins of Fe atoms are obviously asymmetric, and the upper and lower spins of other elements are slightly different, but they are basically symmetric, indicating that the magnetic moment of the alloy is mainly contributed by iron atoms.

This paper calculates the population, electronic charge and magnetic moment of all atoms in Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$, as shown in Table 2. Table 2 shows that the distribution of electrons in different orbits
and the magnitude of the magnetic moment of each iron atom are different. This may be because the distance between the iron atom and the surrounding atoms is different, which leads to mutual coupling with each atom and lattice distortion. Table 2 shows that the total magnetic moment of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ is 84.15 $\mu$. Among them, the magnetic moment of B atoms is -0.16 $\mu$, the magnetic moment of Cu atoms is -0.17 $\mu$, the magnetic moment of Si atoms is -1.16 $\mu$, the magnetic moment of Nb atoms is -3.11 $\mu$ and the magnetic moment of Fe atoms is 88.75 $\mu$. Therefore, it can be concluded that Fe atoms play a decisive role in the magnetic moment of the entire alloy, which is also consistent with the conclusion drawn from the previous analysis of the spin state density.

### Table 2 Atomic charge and magnetic moment of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$.

| Atom | Electron in orbit | Charge/e | Spin/\(\mu\) |
|------|-----------------|----------|--------------|
|      | s    | P     | d     | Total |          |          |
| B    | 0.56 | 1.18  | 0.00  | 1.74  | -0.56   | -0.08    |
| B    | 0.57 | 1.16  | 0.00  | 1.72  | -0.52   | -0.08    |
| Cu   | 0.48 | 0.58  | 4.85  | 5.91  | -0.89   | -0.08    |
| Cu   | 0.46 | 0.54  | 4.86  | 5.86  | -0.82   | -0.09    |
| Si   | 0.65 | 1.28  | 0.00  | 1.93  | -0.02   | -0.17    |
| Si   | 0.65 | 1.32  | 0.00  | 1.97  | -0.07   | -0.15    |
| Nb   | 1.34 | 2.39  | 1.78  | 5.51  | 1.34    | -0.64    |
| Nb   | 1.30 | 2.75  | 1.88  | 5.93  | 0.62    | -0.52    |
| Fe   | 0.41 | 0.27  | 4.22  | 4.90  | -0.01   | 1.79     |
| Fe   | 0.39 | 0.27  | 4.26  | 4.92  | 0.02    | 1.86     |
3.3 Elastic constant

For the optimised Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$, first-principles DFT is still used to calculate its elastic constant $C_{ij}$. Since the crystal structure of the Fe-based nanocrystalline alloy belongs to the cubic crystal system, its mechanical stability is only related to the values of elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. The elastic constants of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$, which were calculated, are shown in Table 3.

| C$_{11}$ | C$_{12}$ | C$_{44}$ |
|---------|---------|---------|
| 133.3397 GPa | 115.4345 GPa | 119.0811 GPa |

The elastic constant determines the mechanical stability of the material. Judging by the mechanical stability of cubic crystals [15]:

$$C_{11} > 0, \quad C_{44} > 0, \quad (C_{11} - C_{12}) > 0, \quad (C_{11} + 2C_{12}) > 0$$

it can be seen that Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ meets the mechanical stability. According to the theory of elasticity [16], for the cubic crystal structure, the elastic constants satisfy the following equations:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (1)$$
$$G = \frac{3C_{44} + C_{11} - C_{12}}{5} \quad (2)$$
$$E = \frac{9GB}{3B + G} \quad (3)$$
$$\mu = -1 + \frac{E}{2G} \quad (4)$$

where $G$ is the shear modulus, $B$ is the body modulus, $\mu$ is Poisson’s ratio and $E$ is Young’s modulus.

Generally speaking, if the material’s $B$, $G$ and $E$ are larger, the hardness of the material is stronger. According to calculations, the body modulus $B$ is 127.3713 GPa, $G$ is 20.1133 GPa and $E$ is 57.3226 GPa, indicating that the iron-based nanocrystalline alloy Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ has a relatively strong resistance to deformation and high hardness. Poisson’s ratio $\mu$, also known as the transverse deformation coefficient, can be used to reflect the ductility and brittleness of materials, just like Cauchy pressure. According to the criterion of mechanical theory, when $\mu < 1/3$, the material is brittle. The calculated $\mu$ is 0.425, indicating that the alloy has better flexibility. In order to further study the mechanical properties of Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$, the ductility and brittleness of the material can be judged according to the ratio of the bulk modulus $B$ and the shear modulus $G$. When the ratio $B/G$ is greater than 1.75, the material exhibits toughness. When the ratio $B/G$ is less than 1.75, the material exhibits brittleness. The calculated ratio $B/G$ is 6.3327, indicating that Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$ has very strong toughness, which is also consistent with the conclusion drawn by Poisson’s ratio $\mu$.

4 Conclusions

This paper uses the first-principles calculation method. The Fe-based nanocrystalline alloy Fe$_{80}$Si$_{10}$Nb$_6$B$_2$Cu$_2$’s crystal structure, energy band structure, elastic constant, magnetic moment and density of states were calculated and analysed, and the following conclusions were obtained:

1. The Fe-based nanocrystalline alloy of this composition has a relatively stable structure and can be used in actual industrial development.
2. The energy band structure of spin-up and spin-down is basically the same, and the energy gap is 0, showing metallic. The band structure dispersion is obviously different, indicating that the Fe-based nanocrystalline alloy has spin splitting and is very magnetic.

3. The electron density of the spin-up and spin-down states is asymmetric near the Fermi level, indicating that the alloy is ferromagnetic. The magnitude of the magnetic moment is 84.15 $\mu$, and the Fe element plays a decisive role in the magnetic properties of the alloy.

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