Effects of Alloying Elements on Mechanical and Electronic Properties of Cu by First-Principles Calculations

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Abstract. The effects of alloying elements (Mn, Cr, Sn, P, Be and Ti) on the mechanical and electronic properties of Cu have been investigated performing first-principles calculations. A supercell consisting of 107 Cu atoms and one solute atom is used. The calculated results show that the binding energy values of Cu107X alloys are negative, indicating they have thermodynamic stable structures. The ductility properties and hardness of Cu and Cu107X alloys are also determined based on the calculated elastic constants (cij’s). It is found that the ductility properties of Cu107X alloys decrease due to the addition of alloying elements, but they still exhibit plasticity. However, the Vickers hardness of Cu107X alloy is improved, and the Cu107Be has the largest calculated value of 5.62 GPa. In addition, the electrical conductivity of Cu107X alloy is reduced, among them, Cu107Be and Cu107Mn have relatively high electrical conductivity of 2.58 and 2.53*10^7 S/m, respectively.

Keywords: Copper Alloys; First-Principles Calculations; Mechanical Properties; Electrical Conductivity.

1. Introduction

Copper and its alloys are widely used in machinery manufacturing, transportation, electric power and other fields [1-2]. Especially in the electronic information industry, copper wire is regarded as an important basic material for electronic packaging due to their excellent electrical conductivity [3-4]. Nowadays, with the rapid development of the microelectronics industry, it is required that the bonding copper wire has more excellent mechanical properties and electrical conductivity. However, high strength and high electrical conductivity are mutually exclusive in nature; therefore, the contradictory relationship must be considered between the properties in the design of the alloy [5]. Research suggests that the solid solution of alloying elements into the Cu matrix usually cause lattice distortion, which improves the mechanical properties of the alloy, but increases the scattering of conducting electrons and impairing the electrical conductivity of Cu [6]. So, how to improve the strength of copper alloys while ensuring good conductivity is one of the important research directions of copper alloys [7]. In order to solve the above problems, various strengthening processes such as alloying, deformation strengthening,
and composite materials method, etc, have been proposed, thus, alloys having high strength and high conductivity such as Cu-Zr, Cu-Cr, and Cu-Re were prepared [8-10].

Although very reliable experimental results can be obtained according to conventional research methods, but it takes a lot of time and cost. Therefore, theoretical prediction for the effects of alloying additions on Cu from the first principles can provide essential guidance in identifying materials with desired mechanical and electronic properties. In the present work, the first-principles calculations are conducted to systematically study the mechanical properties and electrical conductivity of Cu dilute alloys with the addition of elements X (Mn, Cr, Sn, P, Be and Ti).

2. Details of the calculations
In this paper, the first-principles calculations of trace element doping of copper were performed with CASTEP (Cambridge Sequential Total Energy Package) package based on the density functional theory (DFT) ultra-soft potential plane wave method [11]. In the calculation process, the Perdew-Burke-Emzerhof (PBE) potential function in generalized gradient approximation (GGA) is applied to describe the electronic exchange correlation energy part [12], and the convergence calculation is performed by self-consistent field (SCF) method. The accuracy is set to 5.0×10^{-7} eV/atom. In order to suffice the accuracy of the calculation and increase the calculation speed, all calculations are performed in the reciprocal K space. After a series of convergence tests, the Monkhorst Pack [13] 4x4x4 mesh was used in Brillouin zone (BZ) integration, and the plane wave truncation can be set to 450 eV. The crystal structure was geometrically optimized using the Brodyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [14], before all calculations were performed to obtain the most stable structure in the local area. The convergence parameters are setting as follows: The convergence accuracy of the total energy of the system is 5.0x10^{-6} eV/atom, the atomic average force is less than 0.1 eV/nm, the tolerance offset is less than 5.0x10^{-7} nm, and the maximum stress deviation is 0.02 GPa.

Cu belongs to a face-centered cubic (FCC) structure with space group of Fm-3m, a lattice constant of a=b=c=3.6146 Å, and α=β=γ=90° [15]. Subsequently, supercell model consisting of 3x3x3 arrangement of Cu crystal and having 108 atoms was used to simulate the doping of trace X (Mn, Cr, Sn, P, Be, Ti) atoms in Cu for the current calculations, in which the alloying element X replaces the top-corner sites. After the substitution of the X atom, the doped alloy is represented by Cu_{107}X, wherein the X content is 0.926 at%, and the crystal structure is as shown in Fig. 1.

![Figure 1. Supercell model of atom doping Cu with X (Mn, Cr, Sn, P, Be, Ti)](image)

3. Results and discussions
3.1. Thermodynamic Stability
In order to evaluate the stability of doped Cu_{107}X alloys with respect to the Cu_{108} solid, we study their thermodynamic properties by calculating the formation enthalpy and binding energy. Here, the formation enthalpy is used to characterize the energy released/absorbed by different types of atoms from
the elemental state-generating compound, and the easier the formation of the compound if it has the smaller value. The resulting is expressed as \( \Delta H_f \) and is calculated as follows [16]:

\[
\Delta H_f = \frac{E_{\text{tot},X}^{\text{Cu}} - aE_{\text{solid}}^{\text{Cu}} - bE_{\text{solid}}^{X}}{a + b}
\]

where \( E_{\text{tot}} \) is the total energy of the supercell, \( a \) (or \( b \)) refers to the number of \( \text{Cu} \) or \( X \) atoms in the supercell, respectively. \( E_{\text{solid}}^{\text{Cu}} \) and \( E_{\text{solid}}^{X} \) denote the energies per atom of \( \text{Al} \) and \( X \) in the solid states, respectively.

The binding energy is interpreted as the energy released when free atoms are combined into a crystal. The larger the absolute value, the stronger the binding force between atoms in the crystal, indicating that the structure of the compound is more stable. The binding energy is expressed as \( \Delta E_{\text{coh}} \) and is defined as [16]:

\[
\Delta E_{\text{coh}} = \frac{E_{\text{tot},X}^{\text{Cu}} - aE_{\text{atom}}^{\text{Cu}} - bE_{\text{atom}}^{X}}{a + b}
\]

Where \( E_{\text{atom}}^{\text{Cu}} \) and \( E_{\text{atom}}^{X} \) are the energies of \( \text{Cu} \) and \( X \) atom in the isolate state, respectively.

According to the Eq. 1-2, the calculation results of the formation enthalpy and binding energy of \( \text{Cu}_{108} \) and \( \text{Cu}_{107}X \) are shown in Table 1. It can be readily seen that \( \text{Cu}_{108} \) is a simple substance, and the \( \Delta H_f \) is 0 eV-atom\(^{-1}\). After the \( X \) atom is doped, the \( \text{Cu}_{107}X \) alloy has a small enthalpy of formation, and they are easy to form. Among them, the formation enthalpy of \( \text{Cu}_{107} \text{Mn} \) and \( \text{Cu}_{107} \text{Be} \) alloys is negative, expressing that they are easier to form than \( \text{Cu}_{108} \) and other \( \text{Cu}_{107}X \) (Cr, Sn, P, Ti) alloys. The calculated binding energy of \( \text{Cu}_{108} \) is -3.6644 eV-atom\(^{-1}\), which is only 5% deviation compared with experimental value of -3.49 eV-atom\(^{-1}\) [15], suggesting that the calculations in the present work are reasonable. Meanwhile, the calculated binding energy of \( \text{Cu}_{107}X \) alloy is negative, revealing that they all have thermodynamic stability. It is noticeable that the calculated binding energies of \( \text{Cu}_{107} \text{Mn} \), \( \text{Cu}_{107} \text{P} \) and \( \text{Cu}_{107} \text{Ti} \) alloys are -3.6729, -3.6765 and -3.6786 eV-atom\(^{-1}\), respectively, which are smaller than \( \text{Cu}_{108} \), so they have a more stable crystal structure than \( \text{Cu}_{108} \), and \( \text{Cu}_{107} \text{Ti} \) is the most stable. On the contrary, the calculated binding energies of \( \text{Cu}_{107} \text{Cr} \), \( \text{Cu}_{107} \text{Sn} \) and \( \text{Cu}_{107} \text{Be} \) alloys are all larger than \( \text{Cu}_{108} \), so their crystal structure stability is slightly worse than \( \text{Cu}_{108} \). The absolute value of the experimental values of the binding energies of pure metals Mn, Cr, Sn, P, Be and Ti is ranked as Ti>Cr>P>Be>Sn>Mn [15], and it can be found that the structural stability of \( \text{Cu}_{107}X \) is largely affected by the stability of the metal \( X \) itself. However, the doping of Cr and Mn elements does not conform to the above rule, which probably caused by the different crystal structure of Cr and Cu. Doping causes Cu to generate large lattice distortion, which requires more energy to be absorbed during the formation. Mn and Cu are both face-centered cubic structures, so the thermodynamic stability of \( \text{Cu}_{107} \text{Mn} \) is better.

### Table 1. The calculated results of \( \text{Cu}_{107}X \) alloys unit cell total energy, \( \Delta H_f \) and \( \Delta E_{\text{coh}} \), solid atom and isolated atom average energy

| Phase  | Unit cell energy (eV) | Solid atom energy (eV) | Atom energy (eV) | \( \Delta H_f \times 10^2 \) (eV-atom\(^{-1}\)) | \( \Delta E_{\text{coh}} \) (eV-atom\(^{-1}\)) |
|--------|----------------------|------------------------|-----------------|------------------------------------------|------------------------------------------|
| \( \text{Cu}_{108} \) | -181540.7658 | -1680.9330 | -1677.2686 | 0.00 | -3.6644 |
| \( \text{Cu}_{107} \text{Mn} \) | -180483.798 | -623.0098 | -619.3843 | -0.88 | -3.6729 |
| \( \text{Cu}_{107} \text{Cr} \) | -182258.2712 | -2399.4492 | -2395.1292 | 0.94 | -3.6611 |
| \( \text{Cu}_{107} \text{Sn} \) | -181908.0577 | -2048.7549 | -2044.9999 | 0.49 | -3.6604 |
| \( \text{Cu}_{107} \text{P} \) | -180079.1137 | -218.3445 | -214.3107 | 0.87 | -3.6765 |
| \( \text{Cu}_{107} \text{Be} \) | -180252.7426 | -392.2348 | -389.6937 | -0.63 | -3.6603 |
| \( \text{Cu}_{107} \text{Ti} \) | -181453.3308 | -1593.8376 | -1588.2996 | 0.31 | -3.6786 |
3.2. Mechanical Properties

The mechanical properties of the material are closely related to the elastic constant of the solid [17]. For instance, according to calculating the elastic constant $C_{ij}$ of Cu$_{108}$ and Cu$_{107}$X, combined with the Voig-Reuss-Hill approximation [18], the bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio ($v$) of Cu$_{107}$X alloy can be derived. Moreover, according to the Paugh empirical scheme B/G to evaluate the brittleness of the material, and to predict the Vickers hardness (Hv) of the Cu$_{107}$X alloy by semi-empirical formula [19]. The computational formulas are expressed as follows:

$$B = \frac{C_{11} + 2C_{12}}{3}$$  \hspace{1cm} (3)

$$G = \frac{1}{2} \left[ \frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \right]$$  \hspace{1cm} (4)

$$E = \frac{9BG}{3B + G}$$  \hspace{1cm} (5)

$$v = \frac{3B - 2G}{2(3B + G)}$$  \hspace{1cm} (6)

$$Hv = \frac{1-2v}{6(1+v)}E$$  \hspace{1cm} (7)

According to the above formulas, the calculation results are lists in Table 2. It is noteworthy that the calculated values of the elastic constant of Cu$_{108}$ are in good agreement with experimental results [20]. According to Born-Huang’s elastic stability theory, there are three independent elastic constants for the cubic crystal. The restriction of the mechanical stability are given as follows [21]: $C_{11}>0$, $C_{12}>0$, $C_{44}>0$, $C_{11} - C_{12}>0$, $C_{11} + 2C_{12}>0$. As shown in Table 2, all of the elastic constants for Cu$_{107}$X alloys satisfy these criteria mentioned above, indicating that they are mechanically stable.

| Phase | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | B (GPa) | G (GPa) | E (GPa) | B/G | $v$ | Hv (GPa) |
|-------|---------------|---------------|---------------|---------|---------|---------|------|----|---------|
| Cu$_{108}$ | 172.0 | 123.2 | 78.5 | 135.5 | 41.4 | 113.0 | 3.27 | 0.365 | 3.73 |
| Cu$_{107}$Mn | 168.4 | 121.4 | 75.4 | 137.0 | 48.3 | 129.8 | 6.11 | 0.355 | 4.11 |
| Cu$_{107}$Cr | 151.0 | 113.4 | 72.7 | 125.9 | 44.1 | 118.5 | 2.85 | 0.343 | 4.62 |
| Cu$_{107}$Sn | 155.7 | 120.3 | 75.2 | 132.1 | 42.4 | 115.0 | 3.36 | 0.355 | 4.11 |
| Cu$_{107}$Fe | 149.1 | 107.9 | 72.5 | 121.6 | 43.9 | 117.6 | 2.77 | 0.339 | 4.72 |
| Cu$_{107}$Be | 147.7 | 109.3 | 71.9 | 122.1 | 42.6 | 114.4 | 2.87 | 0.344 | 4.43 |
| Cu$_{107}$Ti | 154.5 | 107.8 | 78.8 | 123.3 | 48.5 | 128.7 | 2.54 | 0.326 | 5.62 |

The ductility and brittleness of the material can be evaluated by the B/G ratio and Poisson’s ratio $v$ [22]. The material exhibits a plastic property when the B/G value is greater than 1.75, and the bigger the value of ratio is, the better the ductility of the material is. If the ratio is less than 1.75, it is a brittle material. For the Poisson’s ratio $v$, it is reflect the toughness and brittleness of the material. When the value of $v$ is greater than 0.3, the material exhibits plasticity, and the larger the ratio, the better the plasticity of the material. Comparing the B/G value and Poisson’s ratio $v$ of Cu$_{107}$X alloy in Table 2, on the one hand, it can be seen that the B/G value of the Cu$_{107}$X alloy doped with trace elements are between 2.54–3.1, both greater than 1.75. On the other hand, the Poisson’s ratio $v$ is between 0.326 and 0.355 and are greater than 0.3. At the same time, it is easy to compare the B/G value and $v$ value of Cu$_{107}$X, and their influence on the ductile and brittleness of the doped alloy is consistent. In general, the doping of Be element greatly reduces the B/G value and Poisson’s ratio $v$ of Cu, so the plasticity of Cu$_{107}$Be...
alloy is worse than that of other doped alloys. The doping of the other elements has not obviously effect on the B/G value and Poisson’s ratio \( \nu \) of Cu. Therefore, the Cu\(_{107}\)Mn, Cu\(_{107}\)P and Cu\(_{107}\)Ti have good plasticity.

The hardness of a material always plays an important role in its applications, thus it is necessary to investigate the hardness of material. Table 2 lists the calculated Vickers hardness values for Cu\(_{108}\) and Cu\(_{107}\)X alloys. Since the Cu\(_{108}\) used in the calculation is an ideal model, and the defects of the crystal are not considered, the calculated pure copper Vickers hardness value of 3.73 GPa is larger than the experimental value of the annealing state at room temperature in the Ref. [23] of 1.53 GPa. In addition, Zeng [24] reported that the incorporation of Sn, Mn, P, and Be elements will increase the hardness of pure Cu, which is consistent with the calculation results. So, the doping of the Be element greatly increases the hardness of Cu, and the doping of other elements also appropriately increases the hardness of Cu.

3.3. Electrical Properties

In order to study the electrical conductivity of Cu\(_{108}\) and Cu\(_{107}\)X alloys, the kinetic relaxation including NVE and NVT of Cu\(_{108}\) and Cu\(_{107}\)X was first carried out, and the optical conductivity of several frame structures in the kinetic trajectory was calculated. Finally, the Kubo-Greenwood formula was used to calculate the conductivities of Cu\(_{108}\) and Cu\(_{107}\)X. The specific form of the Kubo-Greenwood formula is as follows [25]:

\[
\sigma_i(k, \omega) = \frac{2\pi}{3\alpha \Omega} \sum_{j=1}^{n_b} \sum_{i=1}^{n_b} \sum_{\alpha=1}^{3} \left\langle F(e_{i,k}) - F(e_{j,k}) \right\rangle x \left| \nabla \alpha |\psi_{i,k}|^2 \right( \epsilon_{j,k} - \epsilon_{i,k} - \omega \right) \tag{8}
\]

Here, the parameters in Formula (8) have been described in previous reports [25], so this paper will not introduce. The optical conductivity of Cu\(_{108}\) and Cu\(_{107}\)X alloys is shown in Figure 2. The optical conductivity is used to describe the behavior of the material to excite free electrons after absorbing photons [26]. From Fig. 2, the optical conductivity of Cu\(_{108}\) and Cu\(_{107}\)X alloys is greater than zero when the incident light energy is 0 eV. This is because the metal has no band gap, and even if there is no incident light, a transition from the valence band to the conduction band can occur. The optical conductivity of Cu\(_{108}\) is the largest, and the optical conductivity of Cu\(_{107}\)X alloy is consistent with the change trend of Cu\(_{108}\). The optical conductivity of Cu\(_{107}\)Mn and Cu\(_{107}\)Be is relatively large, while the optical conductivity of Cu\(_{107}\)P and Cu\(_{107}\)Sn is relatively small.

![Figure 2. Photoelectric conductivity of Cu\(_{108}\) and Cu\(_{107}\)X alloys](image-url)

According to the Ref. [25,27], the optical conductivity of the Cu\(_{108}\) and Cu\(_{107}\)X alloys in Fig. 2 at the frequency of 0 eV is extracted, which is the electronic conductivity of Cu\(_{108}\) and Cu\(_{107}\)X alloy, as shown in Fig. 3. The calculated value of Cu\(_{108}\) conductivity is 5.39*10\(^7\) S/m, and the error of pure copper
conductivity $5.8\times10^7$ S/m [28] is 7%. The calculated value is lower than the experimental value due to the selection of correlation function and pseudopotential. From Fig. 2, we noted that the conductivity of Cu is reduced after the X element is doped, which is mainly due to lattice distortion caused by element doping. Among them, the conductivity of Cu$_{107}$Sn is relatively small compared with other alloys, and its value is $1.91\times10^7$ S/m, which is similar to the conductivity of $2.1\times10^7$ S/m when the Sn doping content is about 1wt% [29]. Furthermore, Cu$_{107}$Be and Cu$_{107}$Mn have relatively high electrical conductivity of 2.58 and $2.53\times10^7$ S/m, respectively.

![Conductivity of Cu$_{108}$ and Cu$_{107}$X](image)

Figure 3. Conductivity of Cu$_{108}$ and Cu$_{107}$X

4. Conclusion
In the present work, we have systematically investigated the thermodynamic stability, mechanical properties as well as electronic properties of different alloyed Cu$_{107}$X (X=Mn, Cr, Sn, P, Be and Ti) systems by employed first principles calculation. From the present study, the following conclusions are obtained:

1). The binding energies of Cu$_{107}$X alloys are negative, indicating that they all have a thermodynamic stable structure. Among them, the binding energy of Cu$_{107}$Ti, Cu$_{107}$P and Cu$_{107}$Mn are -3.6786, -3.6765 and -3.6729 eV/atom, respectively, which have a more stable crystal structure than Cu$_{108}$.

2). The ductility of Cu$_{107}$X alloy decreases due to the addition of alloying elements, but they still exhibit plasticity, among which Cu$_{107}$Mn, Cu$_{107}$P and Cu$_{107}$Ti have good plasticity. On the contrary, the Vickers hardness of the Cu$_{107}$X alloy after doping was improved, and the Cu$_{107}$Be has the largest calculated value of 5.62 GPa.

3). The conductivity of Cu$_{107}$X alloy decreased after doping. Among them, Cu$_{107}$Be and Cu$_{107}$Mn have relatively high electrical conductivity, and their values are 2.58 and $2.53\times10^7$ S/m, respectively.

4). Considering comprehensively, the doping of Be element can improve the mechanical properties of Cu alloy and have less influence on its conductivity.

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