First-principles investigation of site preference and diffusion behaviors of carbon in copper

Hong-Bo Zhou *, Yu-Hao Li, Shuo Jin, Ying Zhang, Xiaolin Shu

Department of Physics, Beihang University, Beijing 100191, China

ABSTRACT

Using a first-principles method, we have investigated site preference and diffusion properties of carbon (C) in copper (Cu). A single C atom energetically prefers to occupy the octahedral interstitial site (OIS) instead of the tetrahedral interstitial site. Double C atoms tend to be paired up at the nearest neighboring OIS's along the $\langle 100 \rangle$ direction mediated by a bridging Cu atom with a distance of 3.85 Å and a binding energy of 0.15 eV. This suggests that an indirectly attractive interaction between C atoms exists, which might lead to a local higher concentration of C in Cu. We demonstrate that the OIS → OIS path is the optimal diffusion path of C in Cu with diffusion barrier of 0.93 eV. By the estimation of pre-exponential factor according to a classical thermodynamics model, the diffusion coefficient as a function of temperature has been determined, which is 3.68×10^{-15} m²/s at a typical temperature of 600 K. The results provide a good reference to understand the behavior of C in Cu.

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1. Introduction

Energy shortage is considered to be the most important problem mankind faces, and nowadays great efforts have been made to develop new kinds of energy resources. One of them is nuclear fusion energy, which is a clean and infinite energy resource for future generation. Fusion energy is being developed internationally via the International Thermonuclear Experimental Reactor (ITER) Project [1], which aims to demonstrate the extended burn of deuterium–tritium plasma in a fusion reaction. The final application of nuclear fusion energy is mainly dependent on the development of key materials in the thermonuclear fusion device "Tokamak", in which the choice of the heat sink material (HSM) is one of the key issues. Due to their high thermal conductivity, high mechanical strength and good radiation resistance [2–5], copper (Cu) and Cu alloys are considered to be the most promising candidates for HSM, in which carbon (C) is regarded as one of the most frequent impurity atoms. Consequently, exploring the interaction between C and Cu not only greatly helps us to understand the effects of C on structure and properties of Cu, but also has a direct impact on the design and operation of a fusion reactor [1].

The interaction of C with metallic atoms is of not only scientific interest but also of technological importance [6–9], as it has a broad range of implications in the materials physics field. In previous theoretical and experimental studies, C has been found to interact strongly with some metals and metal-alloys [10–14]. In Fe–Cu–C alloys, the Cu–C–vacancy clusters can prevent the formation of Cu precipitate crystalline structure under neutron irradiation [14]. Below the C solubility limit, the interstitial C can change the thermal and mechanical properties significantly [11,12]; while above solubility limit, C can easy form carbides, which are useful for improving the strength and the hardness of metals such as steel. The stability of the Cu matrix composites with carbon has been investigated in previous studies [15–20]. It is found that the substitutional impurities can significantly influence the diffusivity of C in the Cu matrix, and zirconium is predicted as the best alloying element for preventing the diffusion of C in Cu–C alloy [15]. A small amount of C in Cu will lead to strong deformation of the Cu host matrix in the vicinity of C [18]. High-resolution scanning electron microscopy results demonstrate the existence of a solid zone at the Cu–C interface [19].

Experimental studies show that the concentration of C is close to appm orders of magnitude in Cu [21–24]. Although C is present only very small amount in Cu, it is expected to play a key role in the structures and the mechanical properties of Cu. On the one hand, C can be easily trapped by some extend defects such as vacancies, grain boundaries and dislocations. The segregation of C at defects will change the Cu microstructure significantly and lead to the degradation of the mechanical properties. This is similar to the effects of hydrogen (H) [25,26], helium [27], sulfur [28,29], and phosphorus [25] on metals. On the other hand, interstitial C diffusion can

also give rise to some problems such as erosion and strain aging [11]. Most importantly, it is found that C act as a trapping site for H isotope ions in Cu [21,22,30], further leading to H bubbles formation, which can seriously influence the microstructure and mechanical properties of Cu, and limit the lifetime of Cu-HSM [31–33].

Previous studies indicate that the interaction between C and Cu plays an important role in the properties of Cu materials. Yet many fundamental aspects underlying the C–Cu interaction have not been well understood. In order to further understand the behavior of C in Cu, in this paper, we investigate the structure, energetics and diffusion of C in Cu using the first-principles method. These results will not only be quite helpful to understand the interaction of C with Cu but can also be viewed as the first step towards studying the effects of C on H bubble nucleation in Cu.

2. Computational method

Our first-principles calculations were performed using the pseudopotential plane-wave method implemented in the Vienna Ab-initio Simulation Package (VASP) code [34,35] based on density functional theory. We used the generalized gradient approximation of Perdew and Wang [36] and projected augmented wave potentials [37], with a plane wave energy cutoff of 400 eV. A fcc Cu supercell of 108 atoms was used, and their Brillouin zones were sampled with $(3 \times 3 \times 3)$ k-points by the Monkhorst–Pack scheme [38]. The calculated equilibrium lattice constant is 3.63 Å for fcc Cu, in good agreement with the corresponding experimental value of 3.61 Å [39]. Both supercell size and atomic positions are relaxed to equilibrium, and energy minimization is continued until the forces on all atoms are converged to less than 10^{-3} eV Å^{-1}.

3. Results and discussions

3.1. Site preference of C in Cu

In order to find the most favorable site of a C atom in the bulk Cu, we examine the solution energies of all potential sites for C, including substitutional and interstitial cases. In a fcc Cu, all the substitutional sites are equivalent, while there are two possible interstitial sites, i.e., octahedral and tetrahedral positions. As shown in Fig. 1, a substitutional site (SS) has twelve nearest neighbors at $0.707a_0$, where a_0 is the lattice constant. The octahedral

interstitial site (OIS) has six nearest neighbors $0.5a_0$, and the tetrahedral interstitial site (TIS) has four nearest neighbors at $0.433a_0$. When the C atom occupies an SS, the solution energy of E_{sub}^{sol} is defined as

$$E_{sub}^{sol} = E_{(N-1)Cu,C} - \frac{N-1}{N} E_{NCu} - \mu(C), \tag{1}$$

where $E_{(N-1)Cu,C}$ is the total energy of the supercell with one C atom at the SS, E_{NCu} is the total energy of an ideal bulk Cu supercell with N atoms, and $\mu(C)$ is the C chemical potential. The C chemical potential $\mu(C)$ is the C energy per atom in the graphite structure. Here, we directly choose the value of -8.01 eV from [11] using first-principles calculations. It is well known that DFT cannot efficiently describe the interaction between the planes in graphite due to the van der Waals forces [11,40,41]. Therefore, we believe that it is basically consistent with the experimental value of -7.37 eV [42]. When the C atom occupies an interstitial site, the solution energy of E_{int}^{sol} can be obtain by

$$E_{int}^{sol} = E_{NCu,C} - E_{NCu} - \mu(C), \tag{2}$$

where $E_{NCu,C}$ is the total energy of the supercell with N Cu atoms and one C atom.

For the substitutional C case, if we consider the high symmetry of the SS, i.e., the C atom is at the center of the substitutional site, a much higher solution energy (3.14 eV) is present in comparison with that of C at the interstitial sites (Fig. 2), implying that the substitutional center is not favorable for the C atom due to its small size relative to the host atom. Thus, only the interstitial sites will be considered in the following studies. For the interstitial C case, here we first consider the high symmetric cases for both the TIS and the OIS, i.e., the C atom stays at the center of interstitial sites. It is found that a single C atom energetically prefers to occupy the OIS with a solution energy of 1.57 eV in comparison with the value of 2.73 eV at the TIS, in good agreement with previous computational results [16,20]. However, provided the C atom slightly deviates from the center of the TIS, it always goes towards the OIS after the optimization of the structure. This suggests that the TIS is not the local energy minimum site for C, but a saddle point, as suggested for C in α-Fe [12].

To further shed light on the physical mechanism underlying the stability of C in Cu, it is helpful to separate the solution energies into two contributions [43]. One is the deformation energy induced by the embedded C atom, defined as the energy release during the course of Cu relaxation after C is removed, and called the mechan-
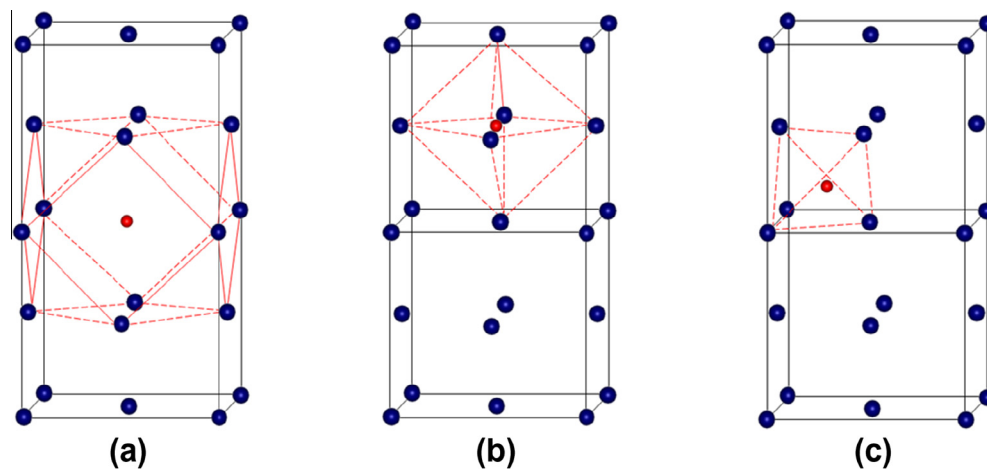
Fig. 1. The substitutional site and interstitial sites in a fcc Cu. (a) Substitutional site, (b) octahedral interstitial site, and (c) tetrahedral interstitial site. The larger blue spheres represent the Cu atoms, and the smaller red sphere represents the C atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)