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Crystallization behaviors and mechanical properties of carbon nanotube encapsulated copper nanowires

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ABSTRACT

Based on the molecular dynamics (MD) simulation, the crystallization behaviors and tensile mechanical properties of carbon nanotube (CNT) encapsulated copper nanowires are investigated in this paper. The influences of the cooling rate, the wall number of CNT and the cross-sectional diameter are considered. It is found that during the crystallization process the CNT acts as a template to induce the nucleation of copper grains from the surface and the template effect is mainly dominated by the innermost layer of CNT via the van der Waals interaction. CNT encapsulated copper nanowire can be formed after the cooling process and the internal copper nanowire is composed of several circumferential fan-shaped polycrystalline grains separated mostly by radial grain boundaries. The crystallinity increases with the increase of the diameter and the decrease of the cooling rate. Tensile tests show that the strength of the composite structure of the CNT encapsulated copper nanowire is much larger than the corresponding pristine copper nanowire. Moreover, it is found that the strength of the composite structure increases with the decrease of the diameter and the CNT plays a dominant role in strengthening the materials. These findings will shed light on the fabrication and practical application of carbon nanotube encapsulated metal nanowires.

1. Introduction

As one of the most important metals, copper and its alloys possess many excellent properties, such as the superior electrical conductivity, corrosion resistance, low cost, and easy casting. The copper based one-dimensional nanomaterials, e.g., the copper nanowire (CuNW), have shown a wide range of applications in various engineering areas [1,2]. However, copper materials usually possess a low strength, which restricts their practical applications in nano-electromechanical systems operated under mechanical loadings. Recently, due to the excellent physico-mechanical properties of carbon nanotubes (CNTs) [3–6], encapsulating metal nanoparticles and nanowires in CNTs becomes an effective way to prepare many novel one-dimensional nanomaterials [7]. For examples, CNTs filled with metal nanoparticles, such as nickel or other transition metals [8–10], can be assembled in various nano-devices and have great potential applications for magnetic media storage, drug delivery, etc. [11–14]. The CuNW/CNT composite structures have also been successfully synthesized by filling copper nanoparticles into CNTs [15] and these materials exhibit tunable electronic properties. The carbon shell provides an effective barrier against the oxidation of the metal [16], ensuring that the encapsulated metal materials remains stable for a long period of time. Moreover, due to the excellent mechanical properties of CNTs, the metal materials encapsulated in CNTs are expected to have enhanced mechanical strength as compared to the pristine metal materials. Until now, various methods have been proposed to fill metals into CNTs, such as the arc-discharge method, electrolytic formation technique and template method [17–20]. However, it is still difficult to control the number and location of fillers in the tube, and the composite structure of fillers and CNTs does not always present the desirable properties. Thus, to guide the preparation of these functional materials, it is very important to understand the mechanism of formation of particles or nanowires in CNTs.

In the past decade, extensively experimental and simulation studies have been performed to investigate the physic-mechanical properties of CNT encapsulated metal materials, such as the compositions, microstructures, electromagnetic properties, and thermodynamic properties. For examples, Lv *et al.* measured the structures and compositions of cobalt and platinum nanowires in CNTs using electron microscopes, and revealed the different growth mechanisms in these systems [21]. Wilson and Madden simulated the growth behavior of potassium iodide in CNTs and demonstrated that the formation mechanism of ionic crystals is

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mainly dominated by intermolecular interactions [22]. They also found that, by controlling the component filling ratio and contact mode, these nanostructures exhibit unusual features. Li *et al.* investigated the filling process of CNTs with nickel atoms using the Monte Carlo method and the results show that the nickel atoms in CNTs exhibit different structural properties as compared to the pristine nickel atoms [23]. Hwang *et al.* studied the diffusion of copper nanoclusters in CNTs using the molecular dynamics (MD) method and found that the nanoclusters migrated rapidly along the tube axis and formed nanowires [24]. Choi *et al.* studied the structure and morphology of CuNWs in the single-walled CNT [25] and their results show that the structure of CuNWs changes from concentric cylindrical shell to face-cubic-centered (*fcc*) lattice with increasing the CNT diameter. These studies provide many insights into the theoretical understanding of the structure-properties relationship and the engineering applications of composite CNT encapsulated metal structures. However, it should be noted that the preparation technology of CNT encapsulated metal composites, especially copper-based composites, is immature, and it is difficult to understand the role of CNT in tailoring the mechanical properties of composite structures from experimental studies. Moreover, only limited simulation studies have been conducted and the structure-properties relationships of CNT encapsulated copper materials have still not been well understood now.

In the present work, MD simulations are carried out to investigate the crystallization behavior of copper atoms in CNTs, including the structural evolution and the mechanisms of solidification. The effects of the cooling rate, the cross-sectional diameter and the number of CNT wall on the crystallization behavior are studied. Furthermore, the mechanical properties of the formed polycrystalline CuNW/CNT composite structures under tensile loading are investigated.

2. Modelling and simulation details

MD simulations are performed to investigate the crystallization behaviors of copper atoms inside various CNTs and the mechanical properties of the composite structures in this work. The copper atoms are initially created as a circular cross-sectional CuNW encapsulated in a CNT, see Fig. 1(a). The length and diameter of the CuNW are l and d, respectively. The periodic boundary condition is applied to the axial direction and a uniform length of l = 6 0.5 Å is chosen in the present work. To describe the interatomic interactions between copper atoms, the embedded-atom method developed by Daw and Baskes [26] and parameterized by Mishin *et al.* [27] is adopted. The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) interatomic potential is used for carbon atoms [28]. In addition, the interaction between the copper and carbon atoms is described by using the Lennard Jones potentials with σ = 3.088 Å and ε = 0.025 eV, where σ is the finite distance and ε is the depth of the potential well [29]. The microstructures in the sample are identified by the common neighbor analysis (CNA) [30] that has the capability to detect whether an atom is in a local *fcc*, hexagonal-close-packed (*hcp*), body-cubic-centered (*bcc*) or the other orders, which are visualized by Ovito [31] and colored by green, red, blue and white, respectively, see Fig. 1. A single layer of *hcp* atoms represents a twin boundary and two adjacent hcp lines are identified as a stacking fault [32,33].

The simulations are conducted by using the LAMMPS code with the velocity-Verlet integrator [34]. The prepared composite structure is first heated up to 1650 K using the velocity rescaling method and then relaxed at 1650 K using the Nosé-Hoover thermostat [35,36] in an NVT ensemble to obtain an initial equilibrium configuration (i.e., a composite structure composed of a perfect CNT and a molten CuNW, see Fig. 1(b)). Since we mainly focus on the crystallization behaviors and the tensile properties of structure, thus the heating rate is chosen arbitrarily. After that, the system is cooling down from 1650 K to 300 K with a specified cooling rate via the velocity rescaling method and relaxed at 300 K via the Nosé-Hoover thermostat to obtain the final crystalized composite structure, see Fig. 1(c). The time step of 1 fs is adopted during the cooling stage. In the tensile stage, the composite structure is first thermally equilibrated at 300 K to obtain a stress-free configuration via a constant NPT ensemble. Then an axial tensile load is applied to the structure by stretching the simulation box along the axial direction with a constant strain rate of 1 ns^{-1} in an NVT ensemble. During the tensile loading stage, the time step is set to 2 fs. To investigate the effects of the cooling rate, the wall number and the diameter of CNT on the crystallization behavior of copper atoms, respectively, three groups of samples are constructed: (1) the double-walled CNT (DCNT) encapsulated CuNWs with a diameter of 193.8 Å are considered, while the cooling rate is chosen as 1, 10, 100 and 500 K·ps^{-1}; (2) the CuNWs with a diameter of 193.8 Å encapsulated by different CNTs are considered, the cooling rate is set to 500 K·ps^{-1}, while four kinds of CNT are selected, that is, the single-walled CNT (SCNT), the DCNT, the three-walled CNT (TCNT) and the four-walled CNT (FCNT); (3) the SCNT encapsulated CuNWs with different diameters are simulated, the cooling rate is also set to 500 K·ps^{-1}, while the diameter d of the CuNW varies as 68.9, 87.1, 127.1 and 193.8 Å.

3. Results and discussion

3.1. Overview of the crystallization behavior of copper atoms in a CNT

To understand the general crystallization behavior of copper atoms in a CNT, the crystallization process of a DCNT encapsulated CuNW with a diameter of 193.8 Å under a cooling rate of 10 K·ps^{-1}

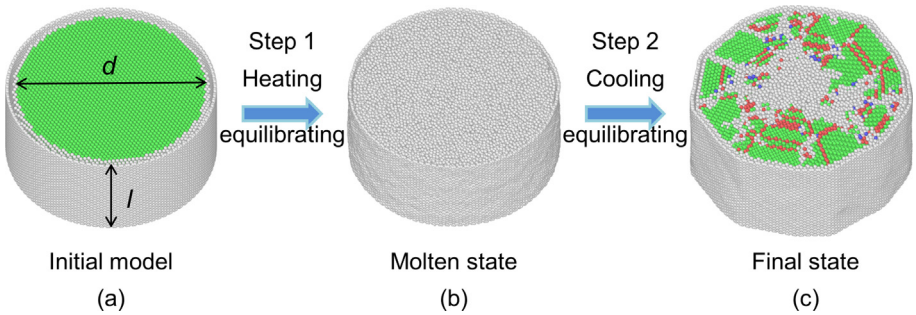

Fig. 1. Schematic plots of the simulated sample at different stages: (a) the initially constructed model, (b) the molten state after heating and equilibrating at 1650 K, and (c) the final crystallization state after cooling and equilibrating at 300 K, in which *fcc*, *hcp*, *bcc* and disordered (i.e., liquid and amorphous) atoms are colored by green, red, blue and white, respectively. The carbon atoms are also colored white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)