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Do Nickel and Iron Catalyst Nanoparticles affect the Mechanical Strength of Carbon Nanotubes?

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ABSTRACT

The growth of carbon nanotubes (CNTs) is strongly mediated by the interaction between Carbon atoms and catalyst nanoparticles, in particular in processes like chemical vapor deposition or floating method. However, the effects these nanoparticles on the mechanical strength of the grown CNTs have remained elusive. Using molecular dynamics dynamic simulations via ReaxFF force fields, the interactions between defect-free single wall CNTs and a series of Nickel (Ni) and Iron (Fe) nanoparticles (NPs) are studied. Pure metal NPs significantly reduce the strength of the CNTs whereas oxidized NPs have more limited detrimental effects. For the same Oxygen content, we also observe that the Fe oxide NPs weaken C-C bonds, i.e. CNTs grown in the presence of Ni particles have higher mechanical strength comparing to those obtained from Fe-based nanoparticles. An analysis of the formation and dissociation of chemical bonds between the C, O, Ni and Fe atoms together with the stress analysis during tensile tests also enable us to elucidate the role of the NPs on the failure mechanisms. The C-C bonds interacting directly with Ni atoms are weakened and therefore control the failure of the CNTs. Surprisingly, the failure of the same CNTs in contact with Fe nanoparticles is driven by the weakening of C-C bonds not directly bonded to Fe atoms.

Keywords

Carbon nanotube; Catalyst nanoparticle; Fracture; ReaxFF

1 INTRODUCTION

Nowadays, carbon nanotubes (CNTs) are embedded in materials in various forms including individual nanofilaments [1]–[4], aerogels [5], fibers [6], [7], grafted [8] or deposited [9] on solid substrates with the objective to improve properties of the matrix and/or fibrous reinforcements they are combined with. Organic polymers [10]–[13] are probably the family of materials which mostly benefited from the intensive use of these nanoparticles with significant improvements of thermal, electrical, and mechanical properties [11], [14], [15]. This trend is, however, less obvious when fiber reinforced polymer composites are targeted. Lab scale experiments incorporating CNTs dispersed in the matrix, deposited around the fibers, or directly grown on the fibers did outline the positive effects of the nano-reinforcements. Upscaling these processes remains, however, challenging [16]–[18]. From this perspective, the continuous fabrication of CNT aerogels based on the “Cambridge process” [5] which can afterward be transformed into fibers (or veils) is one of the most promising approaches to a production of 10-30 m/min [19].

The most extensively used method to synthesize CNTs is the chemical vapor deposition (CVD) process [20], [21] where the catalytic chemical activity of transition metal nanoparticles (NPs) (mostly) deposited on a support promotes the dissociation-diffusion-precipitation mechanism [22], [23]. In this mechanism, the carbon source, mostly in the vapor phase, is first dissociated by metal NPs and the produced carbon atoms dissolve in NPs and finally precipitate to form CNTs. The floating method applied by the Cambridge group relies on the same basic principle except that the CNTs are grown from Fe NPs injected in a solution and “float” in the reactor chamber [5]. The solvent acts as the carbon feedstock.

Regardless of their final form, CVD grown CNTs are mostly obtained from a catalyst metal particle acting as a seed [24]. The most commonly used NPs are composed of transition metals usually Ni, Fe, or Co as well as their oxides and alloys. A low and high adhesion between the substrate and the NP leads respectively to a top-growth mode, i.e. the particle is at the top of the CNTs, and to a bottom-growth mode with a particle positioned on the substrate. Depending on the precise growth conditions, intermediate configurations are also possible with (part of) particles located in the tube. The oxidation state of these particles is not exactly known for their active participation in the CNT growth, especially because the highly reducing environment of the CVD reactor promotes the transformation of metal oxide

NPs into pure metal NPs [25]. This transformation strongly depends on the substrate used [26] as well as the size and the initial oxidation state of NPs.

Generally, NPs are used at a high concentration to favor high yield. Therefore, concentrations of these residual particles in the final CNT material is non-negligible and can amount as high as 30wt. % for the wide-spread HiPco single-wall CNTs [25] or 12wt.% for the floating method [13]. These particles are considered as impurities as they impede the intrinsic electrical and thermal properties of the CNTs. Multiple procedures based on oxidative chemical or physical treatments like ultra-sonication or centrifugation have then been proposed to purify these CNTs, but they remain complicated, un-scalable and can even be detrimental to the CNTs [27]–[30]. However, to the authors' knowledge, there is very little known about the effects of these particles on the mechanical properties of the CNTs. This work aims to address this issue.

Numerous experimental [31]–[33] and modeling [34]–[46] works have been conducted so far almost exclusively without the presence of NPs. A few experimental [47], [48] and theoretical investigations [49]–[59] confirm that Ni and Fe catalyst NPs strongly interact with the structure of CNTs especially when walls are weakened by the presence of vacancies. Increasing the distance between covalently bonded C atoms is an alternative way to weaken them, for example, by imposing a strain along the main direction of the tube. In other words, loading defect-free CNTs in the presence of catalyst NPs would indirectly quantify the detrimental effects of the NPs on their mechanical properties

In conclusion, even though catalyst NPs are indispensable to grow CNTs, only a few atomistic scale observations and quantum chemical calculations have indicated potential modifications of the graphitic structure due to the strong interactions between metal and C atoms. A logical follow-up question concerns the effect of these particles, especially Ni- and Fe-based, on the mechanical performances of the CNTs. Therefore, as a first step, reactive MD simulations predicting the behaviors of 5,5 SWCNTs loaded along the tube direction while in contact with Ni and Fe NPs with different oxidation states have been performed. It was observed that the strength of the CNTs is significantly reduced compared to pristine tubes when pure metal NPs are considered. This detrimental effect was reduced by increasing the oxidation level of the NPs. A detailed analysis of the bond strength between the C, O, Ni and Fe atoms and a stress analysis shed lights on the failure mechanisms and demonstrated

that the two types of metal atoms do not weaken the C-C bonds prematurely in the same way even though the stress-strain curves look similar.

2 SIMULATIONS AND METHODS

The ReaxFF parameter sets used hereafter combines the latest version of the ReaxFFC-2013 parameter set by Srinivasan et al.[60] and the ones developed by Zou et al. [61] to model the interactions between Ni and O atoms. This potential is an extension of the previously published parameters by Mueller et al.[62] for Ni/C/H/O interaction which was trained based on the quantum dataset comprising equation of states (EOS), the heat of formation for Ni and NiC, the binding energies of hydrocarbons on various Ni crystal surfaces, and the binding characteristics of Ni to hydrocarbon fragments. The Ni/O parameters were derived from EOS for Ni and NiO and vacancy formation energy in Ni crystals. This force field has been widely used for modeling of CNT/Graphene and metal/metal oxide nanoparticle interactions [63], [64]. Additionally, C/Fe/O ReaxFF description was acquired by updating the C parameters in the previously developed potential parameters by Shin et al. [65]–[67].

The model systems are composed of an NP positioned in between 2 CNTs (145 Å in length). The distance between the NP and the tubes was fixed to 2 Å to make sure the NP interacts right from the beginning of the simulation with the tubes (Figure 1). A larger distance does not guarantee that the NP stays close to the tubes. It is different from the top, and bottom growth modes as the NP is outside the tube and not inside. This configuration was however chosen as the curvatures of the tubes, and the NP do not match, i.e., it is more difficult for the metal atoms to bond to C atoms. Following the same idea, defect-free 5,5 CNTs were considered, lowering the interactions between the two elements. Such geometry should, therefore, limit the effect of the NP, i.e., all other configurations (presence of vacancies, zig-zag CNT, NP inside the CNT) should show a more pronounced effect. These systems are simplistic, but they contain all the basic ingredients to describe the details of the interactions between the NPs and the CNTs.

To construct the initial structures of both Fe- and Ni-oxide NPs, a hybrid Grand Canonical-Monte Carlo (GC-MC) and MD simulation were utilized. Before the oxidation steps, the pure NPs were equilibrated at room temperature (~300K). Then, the O atoms were inserted into the NPs under $\mu VT N_{\text{Ni/Fe}}$ ensemble, with the constant chemical potential of oxygen (μ_{O_2}), volume (V), Temperature (T) and some iron or nickel atoms ($N_{\text{Ni/Fe}}$). The chemical potential

of O atoms was determined based on the free energy of fictitious reservoir of O₂ with 300 K temperature and $P_{O_2}=10^{-4}$ atm. During the MC trials, O atoms can be randomly inserted into, extracted from or moved into the NPs structure. The potential energy of the system after each MC trial moves is minimized using conjugate gradient (CG) method with a convergence criterion of 0.5 kcal/mol. After every 20 successful GC-MC iterations, subsequent MD runs with 10 ps under isobaric-isothermal condition (NPT) at 300 K temperature and 0.1 MPa pressure were performed to well equilibrate the oxidized NPs. Four Fe-based and three Ni-based particles, namely Fe, Fe₂O, FeO, and Fe₂O₃ and Ni, Ni₂O, and NiO were respectively constructed. The particles were made large enough (between 4.3 Å and 7.7 Å in radius for respectively the Ni and Fe₂O₃ NPs) to avoid the interactions between the tubes and include Ni or Fe atoms not bonded to C atoms. It makes it possible to quantify, during the simulations, the effect of the formation of Fe-C or Ni-C bonds on the Fe-Fe and Fe-O (or on Ni-Ni and Ni-O) bonds.

The tubes were loaded by imposing a constant velocity on the C atoms positioned at the extreme ends of the tubes. A strain rate of 0.2 ns⁻¹ was selected based on the criteria defined by Jensen et al. [68]. The first series of simulations were performed with a time step of 1 fs. Each of these simulations was then restarted at three moderate strains (0.08, 0.10, 0.012) with a time step of 0.5 fs [68] slightly changing the distribution of the initial atom velocities. It is important to repeat the simulations, mimicking an experimental procedure, as failures of the tubes occur catastrophically when a few initial C-C bonds are stretched beyond their maximum length. Small numerical fluctuations might, however, lead to a premature cleavage of the bonds and consequently to bias estimations of the stress and strain at failure. With a minimum of 6 tested tubes per NP, the consistency of the results could be checked and standard errors calculated. The LAMMPS [69] software was used to predict positions, velocities, stresses, and strains in the NVT ensemble using a Nose-Hoover thermostat at 300K. The stresses were obtained via the stress/atom LAMMPS keyword, and the nanotube wall thickness was fixed to 0.34 nm.

Figure 1: Initial configuration of the Fe_2O system. The NP (O atoms in red and Fe atoms in magenta) is positioned in-between the 2 CNTs (cyan and pink) with a distance of 2 Å.

3 RESULTS AND DISCUSSIONS

The results focus first on the prediction of strain-stress curves from which stress and strain at failure can be extracted and the effect of the NPs quantified (Section 3.1). The failure mechanisms are then unraveled by scrutinizing how NP interacts with the nanotubes via a detailed analysis of the bonds formed (bond orders, BOs [70]) between the metal atoms and the C atoms and their effects on the C-C bonds (Section 3.2). Finally, stress and energy analysis is performed (Section 3.3).

Two types of bonds have been defined (Figure 2). First, as the CNT is of armchair type, C-C bonds are oriented at 90° and 30° concerning the loading direction. The evolution of the BOs for these two types of bonds during loading for a pristine CNT, shown in Figure 3, indicates that 30° oriented bonds are weakened during the test whereas the 90° oriented bonds are strengthened. This weakening/strengthening mechanism was observed in all the simulations regardless of the nature and type of NPs. Hereafter, the bond analysis will therefore only focus on the 30° oriented bonds as they are the weakest links in the CNTs.

Also, our observations show that O atoms do not bond to C atoms. Thus, bonding between the NPs and the CNTs is restricted to the formation of Ni-C or Fe-C bonds. We will discuss the energetics of Ni-C and Fe-C bond formations in Section 3.3. Finally, for the bonding

within the nanotubes, two types of bonds were defined: C-C bonds with at least one C atom bonded to one atom of the NP (C_B), and C-C bonds with no C atom directly bonded to the NP (C_{NB}). This distinction between C_B and C_{NB} is crucial to understand how the NPs effectively weaken the C-C bonds especially because the Ni and Fe NPs have distinguishable effects on these bonds.

Figure 2: Definitions of the different bonds analyzed. C_B and C_{NB} refer to C-C bonds with at least one and no C bonded to Ni or Fe atom respectively. 90° and 30° bonds refer to bond oriented at 90° and 30° respectively along the loading direction (indicated by the yellow arrows). The same definitions hold when Fe- and Ni-based NPs are considered.

Figure 3: BO versus strain for the 90° and 30° oriented C-C bonds for a nanotube without NP. Failure of the nanotube occurs at 0.19 strain.

3.1 Mechanical response of CNTs interacting with Ni and Fe-based catalyst nanoparticles

Figure 4 shows stress/strain curves obtained for the simulations restarted at 0.08 strain (the simulations restarted at 0.1 and 0.12 strain show the same behaviors). Between 0.02 and 0.05 strain, the stress levels off even though the systems are continuously loaded. This non-linear behavior is due to a known deficiency of the force fields, but it does not affect the values of the stress at failure and Young's modulus as demonstrated by Jensen et al. [75]. The NPs have an obvious effect on the stress at failure but not on Young's modulus. This latter will therefore not be discussed here. For all the CNTs, the stress is maximum at failure and is therefore equivalent to strength. The system without NP (pristine system) has the highest stress at failure (106.5 GPa at 0.193 strain) and can be considered as the reference system. For the Fe-based NPs, the stress at failure decreases together with the O content in the NPs, the Fe NP having the lowest strength value of 76.1 GPa at 0.137 strain. The same observation can be drawn from the Ni systems for which a minimum strength value of 72.3 GPa at 0.134 strain was obtained. The NiO NP has a peculiar behavior as it does not weaken the tube due to the absence of Ni-C bonds [58]. Figure 5 illustrates the failure of tubes interacting with a Fe₂O and Ni NP respectively.

Figure 4: Stress-Strain curves for the Fe (Left side) and Ni (Right side) systems.

As shown in Figure 5a, the NPs preferentially fail the first tube and then quasi immediately cut the second tube, already weakened, into two parts. The freshly created CNT opened ends either close and form caps when the reactive C atoms do not interact with the NP anymore or are closed by a part of the NPs still strongly attached to these C atoms. A longer time after the CNT failure, the NPs are themselves split into several parts.

Figure 5: (a) Snapshots illustrating the failure of the CNTs in contact with a Fe_2O NP. (b) Snapshots are illustrating the failure of the CNTs in contact with a Ni NP (From left to right

and top to bottom. C atoms are colored in cyan and magenta, and Ni atoms in pink, O atoms in red, and Fe atoms in purple).

Figure 6 summarizes the results of the simulations showing the stress at failure of the CNTs as a function of the NP type. Every data point was obtained by averaging the outcomes of 6 simulations (2 CNTs and three restart times). The relatively small error bars prove the consistency of the results but also evidence significant variation of the strength up to 13 GPa between two simulations of the same system (for the Fe NP). Published results based on a single stress/strain simulation should, therefore, be treated with caution as they might give an inaccurate estimation of the strength of CNTs. The Fe and Ni systems both show the same overall behavior, higher O contents limit the detrimental effect whereas pure metal NPs lower the CNT strength by 29% compared to the pristine case. The strength of the Fe systems almost linearly increases with the increase of the O content in the NP. The Ni systems show a different trend as the NiO NP does not interact with the tubes contrary to the FeO NP. The Ni₂O also shows a less pronounced effect than the Fe₂O NP (89.1 ± 2.7 GPa versus 79.5 ± 2.6 GPa). It is also remarkable that the Fe-based NP always weaken the tubes to a larger extent than the Ni ones. Experimental validations of these results are needed but go beyond the scope of this current study.

Figure 6: Strength of the CNTs as a function of the type of NPs

3.2 Bond analysis

3.2.1 C-Ni and C-Fe bonds

To gain a better insight into the mechanisms involved in the fracture of nanotubes, we first look at the evolution of the number of bonds formed between the metal atoms and C atoms versus strain in Figure 7. The sharp increase of metal-C bonds at the fracture onset indicates the failure of the tubes as the Fe and Ni atoms bonds with the cleaved C-C bonds. Nonetheless, such observation cannot explain why the tubes fail since it should be interpreted as a consequence of the interactions between the NPs and the tubes and not as a cause of their failure. A more detailed analysis of the BOs between the metal and C atoms during loading is necessary to eventually explain the failure mechanisms.

Figure 7: Number of bonds formed between the Fe- (Left side) and Ni-based (Right side) NPs and C atoms versus strain.

As shown in Figure 7 (Left side), throughout the loading, the Fe and Fe₂O NPs are strongly bonded to the CNTs compared to the more oxidized FeO and Fe₂O₃ NPs. Also, the evolution of Ni-C bonds, (Figure 7, Right Side), indicates that pure Ni NP is more bonded to the CNTs than the Ni₂O NP. The NiO NP does not form bonds with the CNTs. It should be noted that the strain level where the major Fe-C and Ni-C bond formation occurs coincidence with the maximum fracture strain in the stress-strain profile (Figure 4). Also, based on Figure 8, on average, 1.78 ± 0.25 Fe-C bonds per C atom with a BO, around 0.48 ± 0.03 are formed for the Fe and Fe₂O NPs whereas only 1.0 ± 0.02 bond with a BO of 0.36 ± 0.03 formed for the FeO and Fe₂O₃ NPs. For these two latter NPs, the Fe-Fe-C triplet has a total BO of 0.72 ± 0.03 (0.36 ± 0.03 for the Fe-Fe bonds, see supporting information, Figure S1, close to the Fe-Fe BO for atoms not bonded to the tubes (0.62 ± 0.04 , supporting information, Figure S2), i.e., Fe atoms bond to the tubes by distributing half of the BO to the newly formed Fe-C

bonds. The Fe-O bonds, with a BO of 0.62 ± 0.04 (supporting information, Figure S2), are then stronger than the Fe-C bonds evidencing the relatively weak interactions between these two NPs and the tubes. The Fe-C BOs for the Fe and Fe₂O NPs (0.51 ± 0.03 and 0.46 ± 0.03) characterize a stronger interaction and therefore alter the distribution of the C-C BOs within the tubes.

Figure 8: Bonding between Fe and C atoms.

Figure 9 shows the evolution of the Ni-C BO and number of Ni-C bonds per Ni atom bonded to a C atom. The Ni-C BO for the Ni NP is not constant during the test and progressively increases from 0.49 to 0.6 till failure of the tubes at a strain of 0.134. For the Ni₂O NP, the Ni-C BO has a constant value of 0.50 ± 0.03 . Above a strain of 0.12, the number of Ni-C bonds per C atom for the Ni and Ni₂O NPs becomes significantly different with values of 1.48 ± 0.16 and 1.04 ± 0.12 respectively. These values are similar to the one obtained for the Fe-based NPs. However, contrary to the case of Fe-based NPs, for these two NPs, the Ni-C bonds are at least as strong as the Ni-Ni and Ni-O bonds (NiO NP) or even stronger for the Ni NP (supporting information (Figures S3 and S4)). These interactions also lead to a modification of the C-C BOs within the tubes.

Figure 9: The evolution of Ni-C bond from the interaction of CNT with pure Ni and NiO nanoparticles during the loading of CNT

In conclusion, the Fe and Ni-based NPs with the higher O contents show relatively weak interactions with the tubes, resulting in a limited effect. The Fe, Fe_2O_3 , and Ni NPs show higher affinities to the tubes evidenced mostly by higher Fe-C and Ni-C BOs. The Fe-C and Ni-C bonds have however significantly different properties which result in specific weakening effects on the C-C bonds of the CNTs as explained in the next section.

3.2.2 C-C bonds

Figure 10 shows the evolution of the C-C BOs for the CNTs interacting with the Fe-based NPs. As already mentioned (Figure 2), the BOs of the C_B and C_{NB} bonds have been independently analyzed. Although the C_B BOs of the tubes interacting with the Fe-based NPs are first lowered compared to a pristine tube, beyond a strain of 0.13, their interactions with the Fe, Fe_2O_3 , and Fe_2O_3 NPs result in higher BOs indicating a strengthening of the C-C bonds. Only the C_B bonds of the nanotubes interacting with a FeO NP are slightly weakened and show a constant linear decrease. The failure mechanism becomes finally clearer when analyzing the C_{NB} BOs as all the tubes have weaker bonds than the pristine case. The CNT/ Fe_2O_3 system has a behavior close to this pristine system which is consistent with an overall moderate effect. The effect on the C-C BOs for the Fe and Fe_2O_3 systems are more pronounced also in line with early failures of the tubes. Once again, the CNT/FeO bonding is characterized by a weak C_{NB} BO, the difference with the reference system being larger than for the C_B BO (-0.09 and -0.05 respectively). The CNTs bonded to the FeO NP therefore also fail due to the weakened C_{NB} bonds like for the three other Fe-based NPs.

Figure 10: BOs of the C-C bonds with C atoms directly (C_B , Left side) and not directly bonded (C_{NB} , Right side) to Fe atoms.

Performing the same analysis for the Ni/CNT systems outlines clear differences between the two types of NPs. Indeed, as illustrated in Figure 11, the tubes interacting with the Ni and Ni_2O NPs fail because the C_B bonds are heavily weakened during loading, with a BO difference with the pristine case at the failure of -0.28 and -0.23 for the Ni and Ni_2O NPs respectively. The C_{NB} BOs are also weakened but to a much lower extent, i.e., the tubes interacting with the Ni NPs fail due to weakening C_B bonds. As expected, the tubes are not affected by a NiO NP, both C_B and C_{NB} matching the pristine case.

Figure 11: BOs of the C-C bonds with C atoms directly (C_B , Left side) and not directly bonded (C_{NB} , Right side) to Ni atoms.

3.3 Corrosive fracture of CNTs using catalyst nanoparticles

Next, we assessed how the aggregation of Ni and Fe atoms in the vicinity of CNTs could alter the stress distribution in the loaded nanotubes. For this, we calculated the stress tensor per atom based on the Virial formalism.

Figure 12: Corrosive fracture of CNT due to interaction with Ni NP. The distribution of axial stress at the onset of crack nucleation. (a) Before and (b) after fracture. The chemical weakening of C-C bonds through the charge transfer from Ni to C atoms (c) before and (d) after fracture.

For the Ni NP, Figure 12a and b display the state of stress right before and after the fracture of the first CNT, respectively. Surprisingly, when the fracture occurs, C atoms interacting with Ni-NP are less stressed than the atoms not interacting with the NP. If the mechanical failure was the dominant mechanisms for fracture of the tube, the cleavage of the first C-C bond and crack-nucleation was expected to happen in the region with highest tensile stress. However, the interaction of Ni and C atoms disturb the stress distribution when at the same time decreasing the chemical strength of the C-C bond. The initial crack formation followed

by circumferential stress redistribution leads to concentration of tensile stress and crack propagation (Figure 12b). It should be noted that the chemical weakening of C-C bonds and crack-tip stress reduction has also been reported in Li-graphene by Yang et al. [71] and Li and CNTs [72] anode systems.

To further explore the coupled chemical weakening and the stress relaxation, we computed and showed the charge distribution corresponding to the same configurations in Figure 12 c and d. It is observed that mediated by the electronegativity difference between carbon (2.52) and Ni/Fe (1.91/1.83), negative charges transferred from the metal to the C-atoms lead to localization of the negative charge in the contact region giving rise to the stress relaxation and chemical bond breaking. An identical analysis was performed for the Fe NP leading to similar observations and conclusions (supporting information, Figure S5).

Figure 13: Energy profile during the dissociation of C-C bond in a pure CNT and a CNT with (a) Ni and (b) Fe adatom approaching toward the center of the highlighted C-C bond. (c) Schematic representation of bond dissociation procedure (d) Comparison between the

dissociation energy pertinent to the direct (yellow) and indirect (Brown) C-C bonds when the Fe ad atom is located at $d = 1.0 \text{ \AA}$

Moreover, bond restraint approach was performed by making a stiff harmonic spring between Ni adatom and a virtual dummy atom in the center of the C-C bond. We consider the bridge site shown in Figure 13c because of its high stability. The equilibrium length of the spring is set to be the initial distance between the Ni adatom and the dummy point in the middle of the highlighted C-C bond (shown in Figure 13c with green particle). Also, the C-C bond length has been increased simultaneously to mimic the cleavage of the C-C bond. The equilibrium distance of the first spring, d is decreased while the C-C bond distance is increased and the equilibrium state of the system is calculated. Then, the energy landscape along the minimum energy pathway, i.e., reaction coordinate, is obtained from the procedure mentioned above and plotted in Figure 13. It is observed that moving the Ni adatom toward the center of C-C bond heavily reduces the energy required for breaking of the C-C bond (Figure 13a). When dissociation of C-C bond in the pure CNT costs around 6.5 eV, incorporation of Ni atom decreases this energy up to $\sim 2.2 \text{ eV}$. As presented by Figure 13b and d, a Fe adatom placed close enough ($\sim 1.0 \text{ \AA}$) to both direct and indirect C-C bonds can weaken the bonds. Especially, the indirect bond is more affected than the direct bond (Figure 13b) by Fe as it is shown in Figure 13d. This bond restraint study together with the previous bond-order analysis indicates that the formation of Ni(Fe)-C bond can negatively affect the strength of C-C bonds in the nanotube.

4 CONCLUSIONS

Using molecular dynamic simulations and ReaxFF force fields, the effects of a series of Fe and Ni NPs on the strength of defect-free SWCNTs have been quantified. The NPs are positioned between 2 identical SWCNTs loaded in tension. The presence of pure metal particles causes them to fail at loads that are 29% lower than those observed for pristine SWCNTs. Oxidized NPs are less detrimental to the nanotubes, in particular, a NiO NP has a negligible effect on the nanotube strength. Both types of NPs show the same trend even though the Fe-based NPs, for any given O content, are more efficient in cleaving C-C bonds. A detailed analysis of the bonds between the NPs and the CNTs, and within the CNTs was performed. The intricate relationships between the Ni, Fe, O, and C atoms were elucidated and then permitted to understand better the failure mechanisms associated with the Fe- and

Ni-based NPs. Indeed, the Fe and Ni atoms do not weaken the C-C bonds in the same way: if the C-C bonds with one C bonded to a Ni atom are significantly weakened, on the contrary, when bonded to a Fe atom, these bonds are strengthened at high strain. The neighboring C-C bonds, with no direct connection with a Fe atom, have a reduced strength and therefore control the failure of the tubes. The FeO NP has a peculiar behavior as both types of C-C bonds are weakened. However, the key C-C bond type remains the one not directly bonded to a Fe atom like the other Fe-based NPs. A detailed stress analysis finally evidenced that the dominant failure mechanism is due to a chemical weakening of the C-C via a charge transfer between the CNTs and the NPs. Although this numerical study investigated model systems and a limited set of materials, the effect of the NPs was identified and eventually explained. Forthcoming studies will focus on the combined effects of common structural defects like the presence of vacancies, of half-walls, and Stone-Walls defect and NPs on the mechanical properties of CNTs.

Notes

The authors declare no competing financial interest.

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