Molecular dynamics simulation of crumpled graphene filled with Ni nanoparticles

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Abstract. Graphene-nickel composites are novel structures with improved properties intensively studied in the last decades. In the present work, molecular dynamics simulation is used to study the process of formation of a composite obtained from well-known crumpled graphene mixed with Ni nanoparticles on the atomistic level. To obtain the composite from initially separated structural units, hydrostatic compression at elevated temperatures is applied. As it is found, the composite structure can be obtained only at high temperatures in 1200 < T < 1500 K range. Numerical tensile tests showed that the higher is the temperature during hydrostatic compression, the smaller is the pore size at the final stage of tension. Compression at high temperature leads to the formation of new chemical bonds between graphene flakes, supports the spread of Ni atoms inside the graphene structure and results in a formation of an excellent composite structure.

1. Introduction
Crumpled graphene is a structure which presents a mixture of graphene flakes (GFs) of different sizes and shapes, crumpled in a different way and connected by van-der-Waals weak interactions. In recent decades it has been considered promising for such applications as supercapacitors [1, 2, 3], hydrogen storage [4, 5], the fabrication of new composite materials [6, 7, 8], to name a few. The success in this field is also connected with the fact that a simple and green approach to obtain crumpled graphene was recently proposed [2].

Recent experiments on the production of graphene-metal composites revealed that such new structures can be obtained by quite simple methods and show much better mechanical and physical properties [9, 10, 11]. However, the experiments were unable to reveal in detail the atomistic mechanisms that govern the composite formation, which can only be realized through molecular dynamics (MD) simulations. This method was previously used for studying different properties of crumpled graphene [12, 13, 4, 5, 14].

In the present work, the fabrication of a graphene-nickel composite by hydrostatic compression is studied by molecular dynamics simulation. This work is a continuation of previous works by the Authors, where the mutual interaction of carbon polymorphs with Ni nanoparticles and also the hydrostatic compression of crumpled graphene filled with nanoparticles were studied [15, 8, 16].
2. Simulation details

The initial structure of crumpled graphene with Ni nanoparticles (NPs) is created by a simple combination of one initial unit to a 3D structure. GF obtained from a 2.5 nm long carbon nanotube (CNT) CNT(15,15): a small part of CNT is cut along the CNT axis. After that, the cut nanotube \( N_C = 252 \) is filled with the Ni nanoparticles \( N_{NP47} \). The diameter of Ni nanoparticles is \( N_{NP47} = 7.2 \, \text{Å} \). Then, the GFs with Ni nanoparticles are randomly rotated, and the structural unit is repeated four times along three directions with the total number of atoms in the system of 19136 with \( N_C = 16128 \), \( N_{Ni} = 3008 \).

To avoid overlapping, the GFs are placed far from each other. Thus, the initial relaxation is not applied since the large pores will not allow the GFs to interact. However, those pores will disappear during further compression. It should be mentioned, that an increase in the size of the computation cell two times does not lead to significant changes in the results. The initial structure of crumpled graphene filled with NPs is shown as a projection on the \( xy \) (a), \( zx \) (b) plane in figure 1.

All simulations have been performed employing the MD package large-scale atomic/molecular massively parallel simulator package (LAMMPS). The potential of the Ni-graphene (\( U_{system} \)) system can be defined as the sum of three potential energies of carbon-carbon (\( U_{C-C} \)), carbon-Ni (\( U_{C-Ni} \)) and Ni-Ni (\( U_{Ni-Ni} \)) interactions, correspondingly:

\[
U_{system} = U_{C-C} + U_{C-Ni} + U_{Ni-Ni} \tag{1}
\]

The adaptive intermolecular reactive empirical bond order potential (AIREBO) [17] is used to describe the interatomic interactions between carbon atoms, which include both covalent bonds in the basal plane of graphene and van-der-Waals interactions between GFs. The AREBO potential has been successfully used to study the deformation behaviour of various 3D carbon systems [13, 14], hydrocarbon structures, hydrogen storage in graphene [18, 5], to name a few.

The second and third terms of Eq. (1) are calculated using the Morse potential

\[
U_{Ni-C}(r) = D_e[(1 - e^{-\beta(r-R_e)})^2 - 1], \tag{2}
\]

where \( D_e \) is the binding energy, \( R_e \) – distance for potential energy minimum and \( \beta \) – potential parameter. The parameters of the Morse potential for describing the interaction of nickel and carbon atoms (table 1) were obtained by the ab-initio method [19, 20, 21].
Table 1. Parameters of the Morse potential.

|         | De, eV | Re, Å | β, 1/Å | Ref.   |
|---------|--------|-------|--------|--------|
| Ni-Ni   | 0.4205 | 2.78  | 1.4199 | [22]   |
| C-Ni    | 0.433  | 2.316 | 3.244  | [19, 20] |

The Morse potential was previously successfully used for the investigation of discrete breathers in two- and three-dimensional crystals [23], studying the martensitic transformation [24], point defects in fcc metals [25], to name a few. Numerous MD simulations of Ni nanoparticles are conducted using parameterization by the embedded atom method for the interatomic potential that reproduces reasonably well the properties of Ni clusters. Although the Morse potential is a simplification of a real system, it can provide results of physical relevance.

The other approach is to study the system by one complex potential. Recently, the parameters for C-Ni were proposed for calculation with the potential of reactive force fields (ReaxFF) [21] using the example of graphene rolls wrapped around a metal nanoparticle. Such type of potential can be used to simulate carbon-based nanomaterials, including other elements, such as H, O, N, S, and some metals, such as Ni, Ag, Au, etc. ReaxFF makes it possible to take into account the contributions to the energy of two-, three- and four-particle interactions, which describe covalent bonds and depend on the bond orders calculated by the empirical formula; take into account the valence of atoms; as well as electrostatic and dispersive contributions. All this determines the high accuracy of calculations. However, previously it was shown that qualitatively results obtained by Morse and ReaxFF are similar and for simplicity, the Morse potential can be effectively used for investigation of a complex system, while ReaxFF is more suitable for studying chemical reactions in a small systems [15, 26].

A constant temperature is maintained by a Nose-Hoover thermostat. The equations of motion for the atoms were integrated numerically using the fourth-order Verlet method with a time step of 0.1 fs.

To fabricate a Ni-graphene composite, the hydrostatic compression $(\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon)$ is applied to the computational cell. The parameter s is increased at a given strain rate. The hydrostatic pressure $p = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, structure density and volume, potential energy and some other characteristics are calculated during deformation.

After compression, the structure and mechanical properties of Ni-graphene composite are analyzed. To study the mechanical behavior, uniaxial tension is applied to the structure, obtained after compression.

3. Results and discussion

To form a strong composite material, the pressure is applied to the initial structure at temperatures $T = (0, 1000, 1200, 1500)$ K, which should activate the formation of new chemical bonds between graphene flakes. It should be noted that this temperature range is rather far from the melting point of graphene (about 5000 K) [27, 28, 29]. In addition, at that temperature nickel nanoparticles would be melted, since the melting point of the nanoparticle is about 1360 K [15]. This will lead to a better distribution of the Ni atoms in the composite structure. Temperatures above 1500 K are not considered because at these temperatures such small clusters of Ni atoms can evaporate.

As it is found previously [15, 8, 16, 26], at zero temperature hydrostatic compression does not lead to the formation of a composite structure. Crumpled graphene filled with Ni nanoparticles can be compressed to high densities of about 6 g/cm$^3$, however, no chemical bonds appear during compression. After uniaxial tension of the compressed structure, the structural elements return to the initial state - separated Ni nanoparticles covered with graphene flakes. At 0 K, Ni NPs preserve the spherical shape, Ni atoms cannot move between different flakes and covalent bonds in the basal plane of GFs cannot be broken at zero temperature. It should be also mentioned, that at room temperature
the formation of a composite is also impossible. Due to this fact only the results for temperature higher than 1000 K are presented in this work.

As an example, figure 2 shows the structural changes under hydrostatic compression at $T = 1200$ K. As can be seen, with an increase in temperature, single graphene flakes change their shape. Some flakes are considerably crumpled which simplified the composite formation. Structural units can rotate and fit each other much better than at low temperatures. Ni atoms can get separated from NP and move to the neighboring flakes or take a place between graphene flakes, which leads to the better mixing in the structure. However, some NPs at 1000 K preserve its initial shape which means that this temperature is also not enough for the transition to the composite state.

In figure 3, the stress-strain curves at uniaxial tension of the composites obtained by hydrostatic compression at elevated temperatures are presented. It should be noted, that hydrostatic tension is conducted at 0 K. As it is found, an increase in temperature positively affects the process of composite formation. At 1500 K, the maximum value of the applied pressure is observed. This can be explained by the fact that at this temperature a sufficient number of additional covalent bonds appear and a greater value of stress is required to break them.
In figure 4, snapshots of the composite structure obtained by hydrostatic compression at 1000, 1200, and 1500 K are presented at different tension strains. The structures withstand high applied tensile pressures about $\varepsilon_{xx} = 0.7$. It can be seen that an increase in temperature leads to better mixing of the elements. At $\varepsilon_{xx} = 0.5$ (T = 1000 K), the first pores begin to appear (figure 4a), and with the strain increase, the size of the pores increases, which is followed by further fracture. As for the structures compressed at 1200 and 1500 K (figure 4b,c), the pores appear a little later. It should also be noted, that the higher the temperature during compression of the structures, the smaller the pore size at the final stage. It can be concluded, that the temperature increase promotes the formation of new chemical bonds. Nearest Neighbour analysis showed that most of the carbon atoms change their hybridisation from $sp^2$ to $sp^3$.

Figure 4. Snapshots of the structure of composite obtained by hydrostatic compression at (a) 1000 K; (b) 1200 K; (c) 1500 K in projection onto the $xy$ plane during stretching. Colors as in figure 1.

4. Conclusions
In summary, molecular dynamics simulation is used to study at the atomistic level the process of formation of a composite structure obtained by hydrostatic compression. From the obtained results it is found that crumpled graphene can be used to obtain a graphene-based composite filled with Ni nanoparticles. Only heating to high temperatures close to 1500 K can affect the transformation of graphene flakes and the formation of covalent bonds between neighboring structural elements. If the nanoparticles inside crumpled graphene are melted, it can ease the process of mixing of Ni and C atoms and lead to the formation of a composite.

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