Hydrostatic compression as the way of property improvement of crumpled graphene: atomistic simulation

K. A. Krylova[1], L. R. Safina[2]

[1]Institute for Metals Superplasticity Problems of the Russian Academy of Sciences, Khalturina 39, Ufa 450001, Russia
[2]Bashkir State University, Validy Str. 32, Ufa 450076, Russia

E-mail: K. A. Krylova bukreevakarina@gmail.com

Abstract. In the present work, crumpled graphene is considered under hydrostatic tension by molecular dynamics simulation. Here hydrostatic compression is used in two variants: to obtain composite from crumpled graphene combined with Ni nanoparticles and to serve hydrogen inside crumpled graphene. Pressure-strain curves and structural transformations during hydrostatic compression in both cases are discussed. It is found, that hydrostatic compression at high temperatures can be very effective for Ni-graphene composite formation. The possibility of application of compressive strain to make crumpled graphene better media for hydrogen storage is discussed. It is observed that at 77 K and 300 K compression results in the considerable increase of hydrogen sorption capacity.

1. Introduction

Nanotechnology is a rapidly developing branch of science, especially if one considers novel carbon nanostructures. Recently, green and effective methods of fabrication a three-dimensional network of crumpled and folded graphene flakes connected by van-der-Waals interactions was proposed by different scientific groups [1, 2, 3]. Such structure derives its name – crumpled graphene (CG) – right from its structural features based on the crumpling of graphene flakes (GF)s. Crumpled graphene demonstrates such properties as the outstanding electrical conductivity of sp^2 GFs, high specific surface area, hierarchical porosity with shortened diffusion pathways, high mechanical strength and flexibility of graphene nanosheets to name a few. Three-dimensional crumpled graphene can demonstrate combined merits from both graphene and porous materials. Possible application of such structures is in different electrochemical energy devices, such as Li-ion batteries, Li-S batteries, supercapacitors, metal-air batteries, fuel cells, water splitting devices, and flexible devices, hydrogen storage. Mechanical properties of CG are of great interest and were previously studied by molecular dynamics simulation [4, 5, 6, 7, 8].

Elastic and inelastic deformation can be considered as a very effective way of changing the physical, sorption, thermal and mechanical properties of carbon nanostructures [9]. High pressure and low temperatures are effective instruments to improve the hydrogen storage capacity [10]. For example, pressure can be used to increase both chemisorption and physisorption [10, 11]. The same approach was used in [12] for pillared graphene bubble system.

In the present work, hydrostatic compression is considered as a promising way to use crumpled graphene as a hydrogen storage media or to obtain new composite material. First,the composite structure with Ni nanoparticles is considered. Simulation is conducted by molecular dynamics simulation. Second, the effect of hydrostatic compression on the capacity of hydrogen storage is presented. Conclusions on the possible practical applications of crumpled graphene are given.

2. Simulation details

The initial structure of CG is presented in Figure 1. This structure is obtained by a combination of GFs to 3D structure where single GF translated as $L_x \times L_y \times L_z$ along x, y and z axis. Each graphene flake is obtained from small carbon nanotube by cut and removing some carbon atoms. The initial structure of CG then was filled with Ni nanoparticles or hydrogen atoms cluster. Let the structure with Ni nanoparticles be mentioned as A and structure with H atoms as B. All the structures are considered at density 1 g/cm^3 because only just at this value structural elements start to interact.
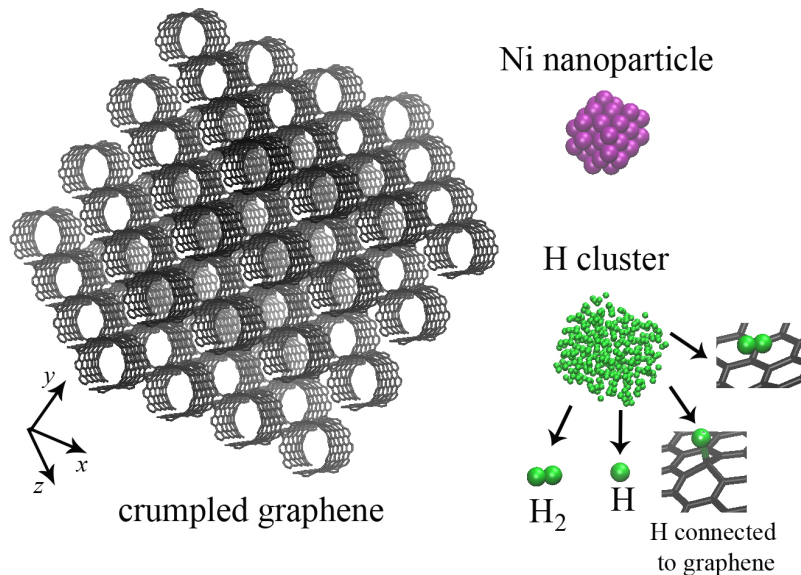

Figure 1. Initial structure of crumpled graphene, Ni nanoparticle, and H cluster. For hydrogen atoms all the possible configurations are presented

The simulations are conducted using a large-scale atomic/molecular massively parallel simulator (LAMMPS) package. Periodic boundary conditions are applied for all cases. As was shown previously, at periodic boundary conditions the size of the simulation cell has no effect on the obtained results [4, 5, 6, 7, 8]. Equations of motion for the atoms were integrated numerically using the fourth-order Verlet method with the time step of 0.1 fs. The Nose-Hoover thermostat is used to control the system temperature.

2.1. Ni-graphene composite

To obtain Ni-graphene composite, Ni nanoparticles N_{Ni}=21, 47, 66, 78 was inserted inside GF N_C=299 and then randomly rotated and translated as 4×4×4 along x, y and z axis. All structural configurations obtained during simulation are shown in Figure 1: single hydrogen atom H, hydrogen molecule H_2, a hydrogen atom attached to graphene and hydrogen molecule attached to graphene.

Simulations are performed using AIREBO potential to describe the interatomic interactions between carbon atoms, which include both covalent in the basal plane of graphene and van-der-Waals interactions between GFs. To describe interatomic interaction for Ni-Ni and Ni-C, Morse interatomic potential is used with parameters D_e=0.4205 eV, R_e=2.78 Å and β=1.4199 1/Å for Ni-Ni [13]; and D_e=0.433 eV, R_e=2.316 Å and β=3.244 1/Å for Ni-C obtained by *ab-initio* simulations [14, 15].

Here, to obtain composite structure, CG with Ni nanoparticles hydrostatically compressed at temperatures 1000$< T <$2000 K, because at this temperature range interaction between GFs is activated. At the same time, the melting temperature of the Ni nanoparticle is about 1300 K. Thus, in temperature range between 1000 K and 2000 K melting of Ni nanoparticle can start facilitate the mixing of the structural components or nanoparticle can be fully melted which leads to even better spreading of Ni atoms inside CG.

2.2. Hydrogenated graphene
Hydrogenated CG consists of 616 carbon atoms and 371 hydrogen atoms and each GF is translated as 3×3×3 along x, y and z axis. The simulation cell for structure B includes 26649 atoms. The simulations are conducted using AIREBO interatomic potential [16] which was previously effectively used for studying carbon nanostructures with hydrogen [17, 18, 19, 20, 21, 22]. However, AIREBO potential has some limitations, for example, for studying discrete breathers in hydrogenated graphene [23, 24, 25] or for investigation of chemical interaction between graphene (carbon atoms) and hydrogen atom [26, 27].

Two temperatures - 77 K and 300 K - are considered. From one hand, it is known that the maximum sorption capacity of hydrogen could be reached at 77 K for different carbon structures [28, 29]. On the other hand, 300 K is also characteristic room temperature at which dehydrogenation can starts.

3. Results and discussion
3.1. Hydrostatic compression for composite fabrication
Hydrostatic compression of the initial structures was carried out at temperatures of 0; 300; 1000 and 2000 K. These studies were carried out in order to ensure the formation of the most durable composite since an increase in temperature leads to the activation of the appearance of new bonds between graphene flakes. In Figure 2, pressure-strain curves for four structures are presented for 1000 K and 2000 K. Curves at 0 K and 300 K are not presented, because at such small temperatures no composite formation is observed.

As can be seen, in the case when Ni nanoparticle is very small (Ni$_{21}$) increase of temperature from 1000 K to 2000 K does not lead to any changes, which can be explained by the fact that at 1000 K small nanoparticle are already melted and easily spread inside graphene flake. Fro the biggest nanoparticle (Ni$_{78}$), curves for 1000 K and 2000 K are also close because, as the analysis of structure showed, at any temperature, this nanoparticle fills the graphene flake and after that structural unit is a rigid metallic sphere covered with graphene. In this case, formation of the composite is difficult. Curves for nanoparticles Ni$_{47}$ and Ni$_{66}$ considerably affected by the temperature increase: the same pressure value is achieved at lower compression strain.

With temperature increase, the interaction between GFs begins much earlier than at zero temperature. This is due to the fact that the flakes begin to rotate due to thermal vibrations, take a different shape, and new chemical bonds between the individual flakes begin to appear actively. Two snapshots of the structure compressed at T=0 K and T=1000 K after ε=0.2 (in Figure 3 b) are presented for comparison. In general, the temperature positively affects the dynamics of the formation of the composite structure.

In Figure 3, pressure-strain curves structures with Ni$_{47}$ nanoparticles under tension are presented. The structure was initially hydrostatically compressed at T=0; 1000; 2000 K. As
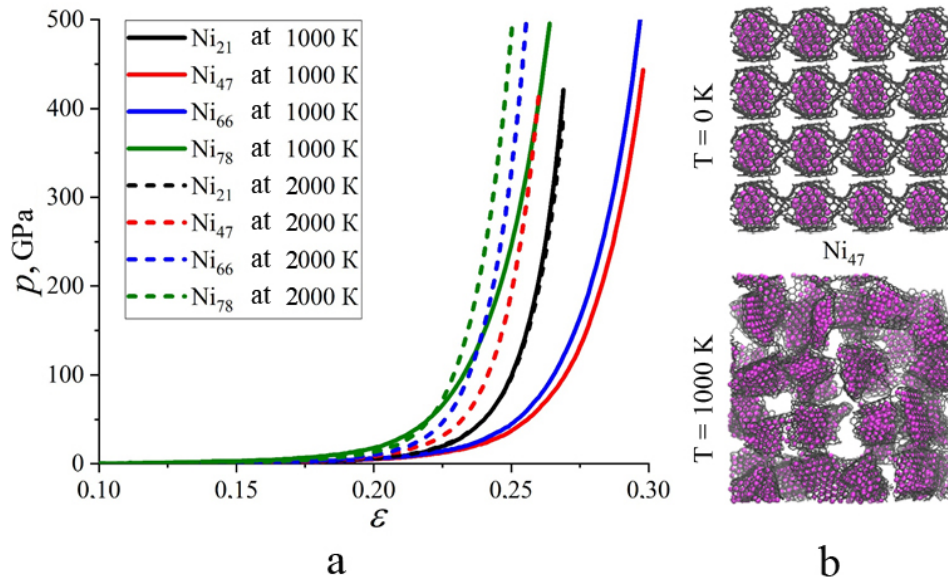
Figure 2. (a) Pressure-strain curves for four types of structures with nanoparticles hydrostatically compressed at temperatures of 1000 K and 2000 K. (b) Snapshots of the structure with Ni_{47} at 0 K and 1000 K at compression ($\varepsilon=0.2$). Colors as in Figure 1

it can be seen, at 0 K stresses under tension increase to about 550 GPa and then stop changing. As it can be seen from the corresponding snapshot, structural elements stay round, almost no chemical bonds appeared between GFs, large pores can be seen even at $\varepsilon=0.3$ and earlier. At higher temperatures, increase of stress is observed with the following small decrease which is more characteristic for composite structure. From the snapshots, mixing of the elements can be seen. At $T=1000$ K, after tension until $\varepsilon=0.3$ small pores are appeared, while after compression at $T=2000$ K, where melting of the nanoparticles and spreading of the Ni atoms inside crumpled graphene took place, mixing is much better.

3.2. Hydrostatic compression for hydrogen storage
At first, it should be noted that initially, only hydrogen atoms introduced to the structure. After several first steps, hydrogen atoms H were mostly transformed into hydrogen molecules H_2. Both hydrogen atoms and hydrogen molecules can be attached to graphene by chemical or Van-der-Waals bonding respectively. All the structural configurations are presented in Figure 1.

In Figure 4a, volumetric density as the function of time at two strain values $\varepsilon=0$ and $\varepsilon=0.4$ for two temperatures $T=77$ K and $T=300$ K are presented. As can be seen, after 2 ps of holding at 77 K or 300 K, increase of strain from 0 to 0.4 results in increase of volumetric density of hydrogen storage. Contradictory to 300 K, at 77 K even holding during 20 ps lead to considerable increase of volumetric capacity. This can be explained by Van-der-Waals interaction between hydrogen molecules and graphene flakes. From the snapshots (Fig. 4b) it can be seen, that H_2 occupies all the empty sites inside GF and some hydrogen molecules attached to the back side of the flake. Since Van-der-Waals interactions can be easily destroyed by thermal fluctuations, this behavior is found only for low temperatures 77-200 K.

4. Conclusions
In this work, hydrostatic compression is applied to crumpled graphene with different filling elements - hydrogen and Ni atoms. The study is conducted by molecular dynamics simulation.
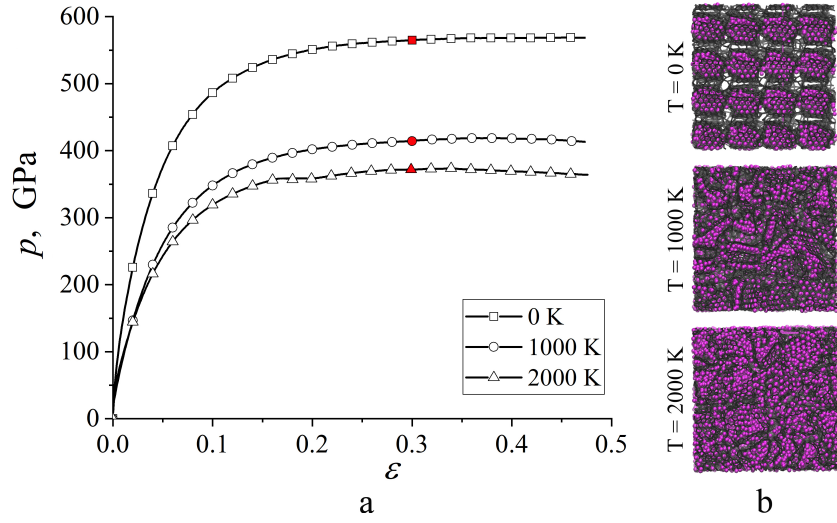
Figure 3. (a) Pressure-strain curves for structures with Ni_{47} nanoparticles under tension. Structure was initially hydrostatically compressed at $T=0$; 1000; 2000 K. (b) Snapshots of the structure with Ni_{47} at $\varepsilon=0.3$ (dot is shown by red on pressure-strain curves). Colors as in Figure 1
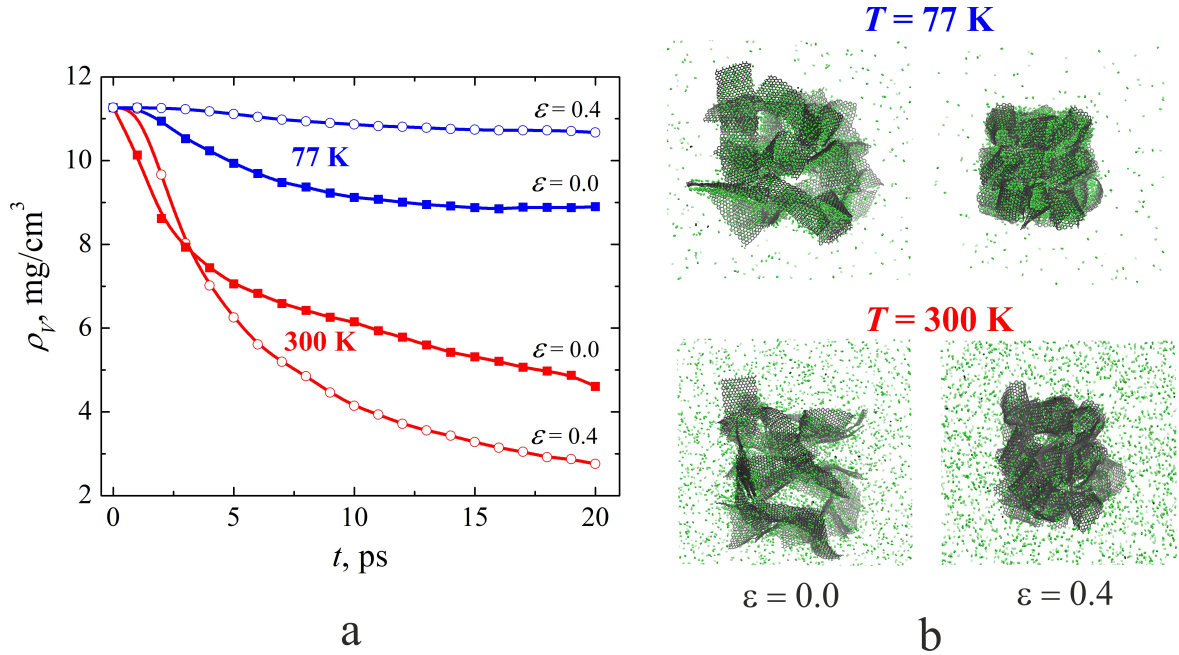

Figure 4. (a) Volumetric density as the function of time at two strain values $\varepsilon=0$ and $\varepsilon=0.4$ for two temperatures $T=77$ K and $T=300$ K. (b) Snapshots of the structure. Colors as in Figure 1.

The possibility of application of crumpled graphene as matrix for composite Ni-graphene structure and for hydrogen storage is discussed.

From the obtained results it is found that crumpled graphene can be used to obtain graphene-based composite filled with Ni nanoparticles. It is observed, that even high pressure up to 500 GPa cannot be successfully used to obtain composite structure at zero or room temperature. Only heating to high temperatures close to 1000-2000 K can affect the transformation of graphene

flakes and formation of covalent bonds between neighboring structural elements. Moreover, the size of the nanoparticle is of high importance: small nanoparticles can be easily melted even at 1000 K, while big nanoparticles stay rigid until 2000 K. If nanoparticle melted, it can ease the process of mixing the elements and lead to composite formation.

The improvement of the hydrogen storage capacity of CG by application of hydrostatic pressure is found at 77 K and 300 K. This work shows that the hydrogen storage capacity of the crumpled graphene can be maximized by decreasing the temperature and increasing the applied hydrostatic pressure. The obtained results can significantly enriched the understanding of the possibility to use graphene-based functional materials for hydrogen storage and transportation.

5. Acknowledgments

6. References

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