Journal of the Korean Ceramic Society
Vol. 54, No. 6, pp. 506~510, 2017.

https://doi.org/10.4191/kcers.2017.54.6.10

Effects of Grain Size Distribution on the Mechanical Properties of Polycrystalline Graphene

Youngho Park and Sangil Hyun†

Simulation Team, Convergence R&D Division, Korea Institute of Ceramic Engineering and Technology, Jinju 52851, Korea

(Received July 31, 2017; Revised October 17, 2017; Accepted October 24, 2017)

ABSTRACT

One of the characteristics of polycrystalline graphene that determines its material properties is grain size. Mechanical properties such as Young's modulus, yield strain and tensile strength depend on the grain size and show a *reverse* Hall-Petch effect at small grain size limit for some properties under certain conditions. While there is agreement on the grain size effect for Young's modulus and yield strain, certain MD simulations have led to disagreement for tensile strength. Song *et al.* showed a decreasing behavior for tensile strength, that is, a pseudo Hall-Petch effect for the small grain size domain up to 5 nm. On the other hand, Sha *et al.* showed an increasing behavior, a *reverse* Hall-Petch effect, for grain size domain up to 10 nm. Mortazavi *et al.* also showed results similar to those of Sha *et al.* We suspect that the main difference of these two inconsistent results is due to the different modeling. The modeling of polycrystalline graphene with regular size and (hexagonal) shape shows the pseudo Hall-Petch effect, while the modeling with random size and shape shows the reverse Hall-Petch effect. Therefore, this study is conducted to confirm that different modeling is the main reason for the different behavior of tensile strength of the polycrystalline structures. We conducted MD simulations with models derived from the Voronoi tessellation for two types of grain size distributions. One type is grains of relatively similar sizes; the other is grains of random sizes. We found that the pseudo Hall-Petch effect and the reverse Hall-Petch effect of tensile strength were consistently shown for the two different models. We suspect that this result comes from the different crack paths, which are related to the grain patterns in the models.

Key words : Polycrystalline graphene, Molecular dynamics, Mechanical properties, Hall-Petch effect

1. Introduction

Graphene has been investigated for its superior material properties using various experimental and theoretical methods.[1] Among these, mechanical properties such as Young's modulus, tensile strength and fracture strain have been investigated mainly by molecular dynamics (MD) calculation. Single crystal properties are rather well examined by MD study[2] as well as quantum mechanical study using ab initio calculation.[3] However, in reality, polycrystalline models are of more interest because fabrication methods such as CVD naturally produce polycrystalline microstructures.

There have been some studies on the mechanical properties of polycrystalline graphene by MD.[4-8] They calculated values for the various mechanical properties and investigated the dependence of those properties on the grain size in order to observe a Hall-Petch effect or reverse Hall-Petch effect in a wide range of grain size. They used either the Tersoff potential or the AIREBO potential to describe the empirical interatomic potential between carbon atoms, and conducted tensile simulation, usually at room temperature (T = 300 K).

†Corresponding author : Sangil Hyun
E-mail : shyun@kicet.re.kr
Tel : +82-55-792-2699 Fax : +82-55-792-2798

Among these studies, there is agreement on the grain size behavior regarding Young's modulus and fracture strain. As the grain size increases, Young's modulus increases and the fracture strain decreases. However, there is a disagreement regarding tensile strength or UTS (ultimate tensile strength). In Song *et al.*'s study,[4] the UTS showed decreasing behavior as the grain size increased, which is the Hall-Petch effect. On the other hand, from other studies,[5,6,8] the UTS showed an increasing behavior as the grain size increased, which is the reverse Hall-Petch effect. We suspect that the main difference between these results might be the size and shape of grains in the models. In the model showing the Hall-Petch effect, the size and shape of grains are rather uniform, but in the model showing the reverse Hall-Petch effect, the size and shape are not uniform. Therefore, the different behavior of UTS may come from the regularity of size and shape of grains. It is necessary to check whether the regularity of size or shape can cause such different behaviors.

In this study, we investigated mechanical properties such as Young's modulus, fracture strain and UTS for various grain sizes. We performed tensile deformation for the polycrystalline model and obtain the grain size behavior of the mechanical properties. For models with a given (averaged) grain size, MD simulations for a few random samples are done for models both with regular sized grains and with random sized grains.

2. Simulation Models and Method

2.1. Modeling

Modeling of polycrystalline graphene was done by Voronoi tessellation method. Each seed is located at the center of each grain and each grain has the form of a polygon, usually with 5 - 8 edges. In general, we choose positions of seeds randomly without any constraint for Voronoi tessellation. Then, the sizes and shapes of the grains are arbitrarily selected as shown in Fig. 1(a).

However, one may want rather uniform sizes of grains; it is possible to make grains size uniform in Voronoi tessellation. We simply apply a constraint when we choose the positions of seeds in the grains. That is, we put a minimum distance between two seeds of grains; this distance is 2r (r: radius of an imaginary circle with area identical to that of the grain). Then, every grain has size larger than 2r. If we choose an r value that is large enough, we have a rather uniform size of grains, as shown in Fig. 1(b). In Fig. 1(a) and (b), all grains have different crystal orientations and there is almost no gap between the grains.

The size of each grain is calculated as the diameters of circles that have the same number of atoms as the grains

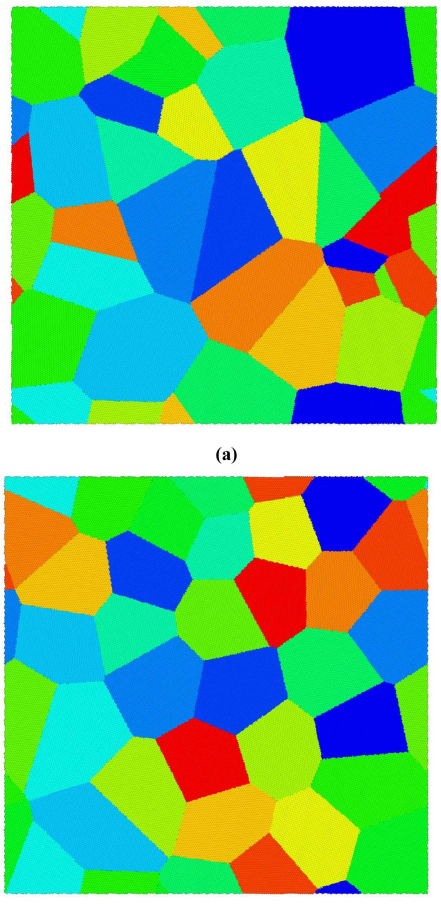

Fig. 1. Modeling of polycrystalline graphene (model of 32 grains) by Voronoi Tessellation (a) with random sized grains (b) with regular sized grains.

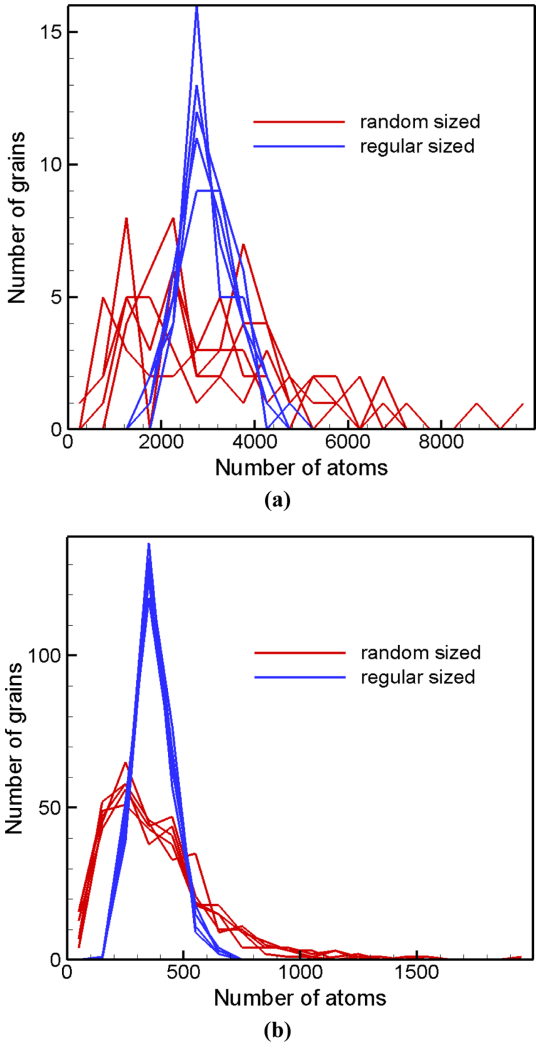

Fig. 2. Grain size distributions of polycrystalline graphene with random sized grains and with regular sized grains; five samples are used for each case: (a) for 32 grains (b) for 256 grains.

have. Since we have fixed the model size at 50 nm × 50 nm, the grain size can be determined by the number of grains. Fig. 2 shows the grain size distributions of polycrystalline samples with random sized grains and with regular sized grains for the models with 32 grains and 256 grains. Here, to achieve better statistics, we generated five different samples for each case. While the distributions are spread with long tails for the random size cases, the distributions are shown as rather sharp for the regular size cases; they could be even sharper by adjusting 2r. If the grain number is smaller than 32, the statistical error is too large, and therefore we performed the simulations for grain numbers equal to or larger than 32. Since the model size is fixed, the largest grain size is 5 nm, which is different from our previous study.[8)]

2.2. Calculation Method

For the prepared polycrystalline models, we performed

tensile deformations in the x direction. We used the NPT ensemble and the Tersoff potentials rather than the AIREBO potential, which was used in our previous study.[8] Initially, the model was relaxed for 100 picosecs and then was deformed at a strain rate of 10^9 sec^{-1} and at room temperature (300 K). We employed an MD simulator for large atomic and molecular systems, LAMMPS.[9]

Since we fixed the model size at 50 nm × 50 nm, the grain size was determined by the number of grains, as mentioned earlier. The number of grains was in the range of 32 to 512, and hence the grain size was in the range of 1.25 ~ 5 nm. For each size, we made five random samples and conducted the simulations for random sized grains and for regular sized grains.

3. Results

3.1. Tensile Deformation

Figure 3 shows before fracture (a, c) and fracture moments (b, d) for the tensile deformations of polycrystalline graphene with 32 grains with regular sized grains in (a, b) and with random sized grains in (c, d), respectively. For both cases, the crack initiations originated from the grain boundaries, where the atoms were excited with high strain energy under the deformations. These cracks can propagate mainly through the grain boundaries until they percolate in the vertical (y) direction, which is orthogonal to the applied tensile (x) direction. However, more than one crack initially exists for the random sized grains shown in (a), and there are more cracks propagating into the inside of the grains for the random sized grains (b) than for the regular sized grains (d). Also, the crack structure is more complicated for the random sized grains, while the crack percolates in a rather simple way for the regular grains.

Stress vs. strain curves for tensile deformation for a few grain sizes (or number of grains) are shown in Fig. 4. The random sized grains are shown in (a) and the regular sized grains are shown in (b). Initially, the slope is small and gradually becomes larger to reach its maximum value at strain values of 0.02 ~ 0.05 for all cases in (a) and (b). The reason for this gradual increase of the slope can be interpreted as the stretching of wrinkles that occurs near the grain boundaries.[5] As the grain number increases, that is, as the grain size decreases, the domain of the slope change becomes wider because the smaller grain size case has more grain boundaries and wrinkles.

As the grain number increases, the slope will decrease regardless of the strain domain that determines it (correspondingly, grain size decreases) for both (a) and (b). Fracture strain also increases for both cases, but fracture strain for regular sized grains in (b) increases more than it does for the random sized grains in (a). UTS is shown to decrease for random sized grains in (a), while it is shown to increase slightly for regular sized grains in (b).

3.2. Young's Modulus, Fracture Strain and UTS

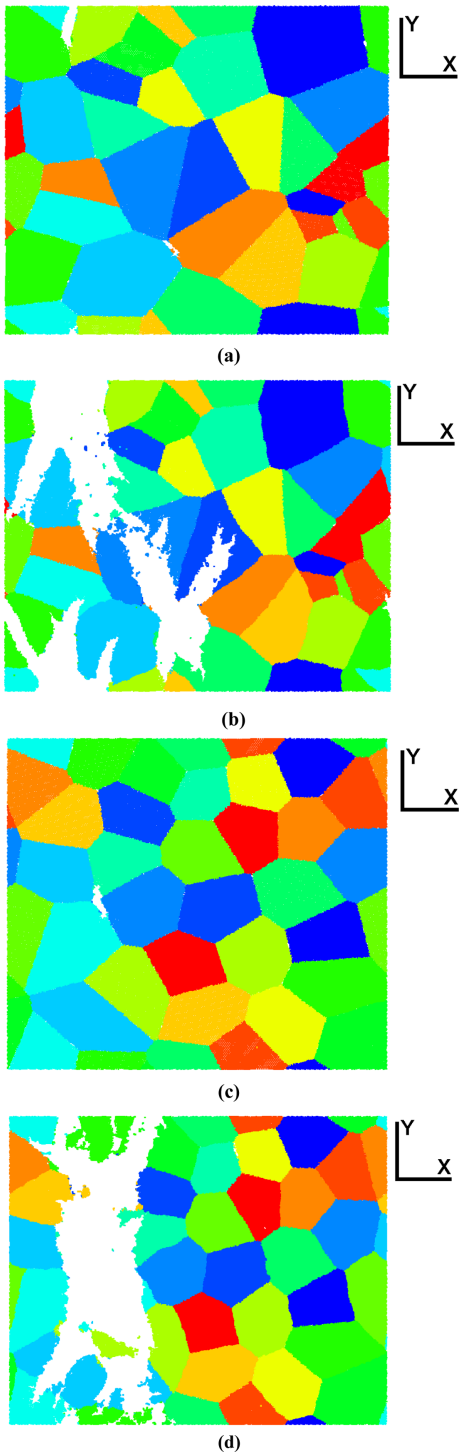

Fig. 3. Before fracture and fracture moments for tensile deformation of polycrystalline graphene of 32 grains: (a, b) with random sized grains, (c, d) with regular sized grains (color denotes different grains).

From the stress vs. strain curves in Fig. 4, we can calculate the Young's modulus, fracture strain and UTS for each grain model with different grain sizes. As mentioned earlier, there are five random grain models for each grain size. Calculations are done both with the random sized grains

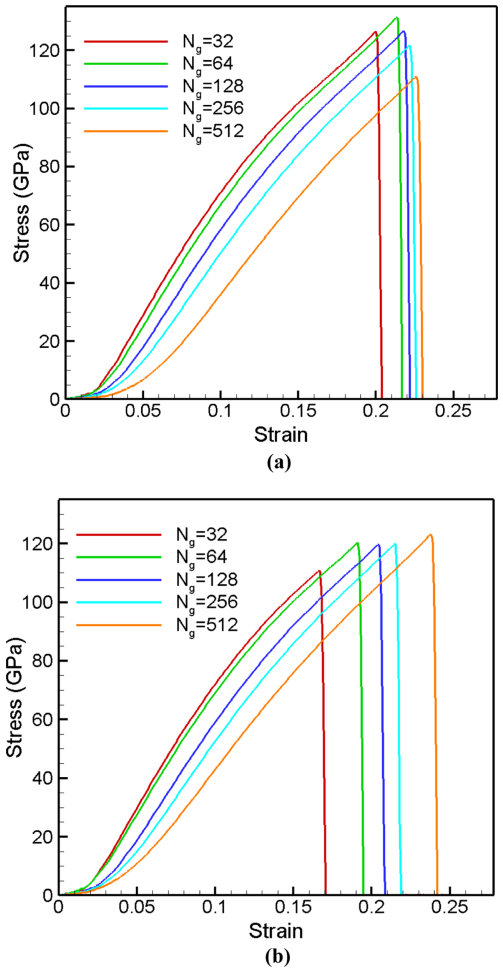

Fig. 4. Stress strain curves of polycrystalline graphene for various numbers of grains: (a) with random sized grains, (b) with regular sized grains.

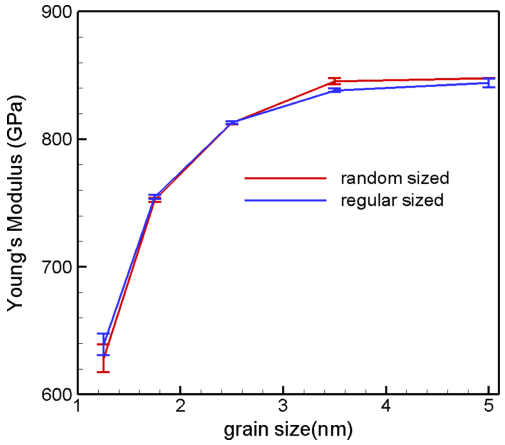

Fig. 5. Young's modulus vs. grain size of polycrystalline graphene with random sized grains and with regular sized grains.

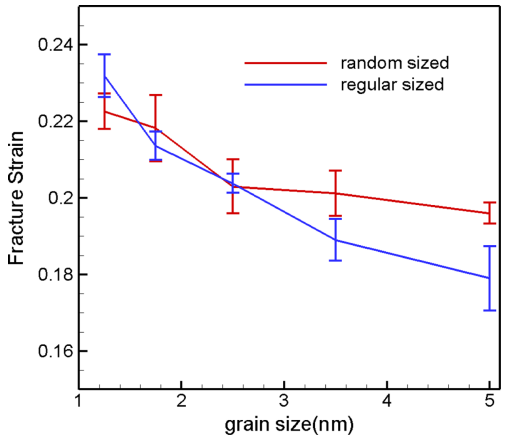

Fig. 6. Fracture strain vs. grain size of polycrystalline graphene with random sized grains and with regular sized grains.

and with the regular sized grains. Fig. 5 shows Young's modulus vs. grain size both with random sized grains and with regular sized grains. Young's modulus was taken as the slope of the stress strain curve in the strain domain between 0.05 and 0.10 in Fig. 3. Young's modulus increases as the grain size increases. The value of Young's modulus was in the range of 600 ~ 850 GPa for the grain size of 1 ~ 5 nm, which is very similar to the results of Song *et al.*.[4] Young's modulus of single crystalline graphene is reported to be around 1 GPa.[2,3] In general, Young's modulus of polycrystals for most materials is somewhat smaller than that of single crystalline. Hence, even for very large grain size, Young's modulus of polycrystals might be under 1 GPa.

Figure 6 shows the curves of fracture strain vs. grain size for both with the random sized grains and with the regular sized grains. As the grain size increases, the fracture strain decreases for both with the random sized grains and with the regular sized grains. This decrease of fracture strain is shown to be faster for the regular sized grains than for the random sized grains. There are more deviations of the grain sizes and more small grains exist for the models with the random sized grains. Then, even for the case with large average grain size, there exist more wrinkles to be stretched and, hence, decrease of fracture strain is slower for the random sized grains.

In Fig. 7, although it can be seen that there is non-negligible fluctuation, UTS increases for the random sized model as the grain size increases. However, in the present study, UTS for the regular sized model seems to decrease slightly or remain nearly constant; further study may be required to clear up this matter. Therefore, both the reverse Hall-Petch effect and the Hall-Petch effect can be seen to appear, which agrees with previous results.[4-6] For regular sized grains, it is easier to find crack paths and the cracks propagate through the grain boundaries as shown in Fig. 3. As the grain size increases, the crack paths may become somewhat simpler; that is why the UTS slightly decreases. On the other hand, for the random sized grains, it is not simple to find the crack paths through the grain boundary, and hence the cracks propagate inside the grains. As the grain size increases, there are still small grains and the

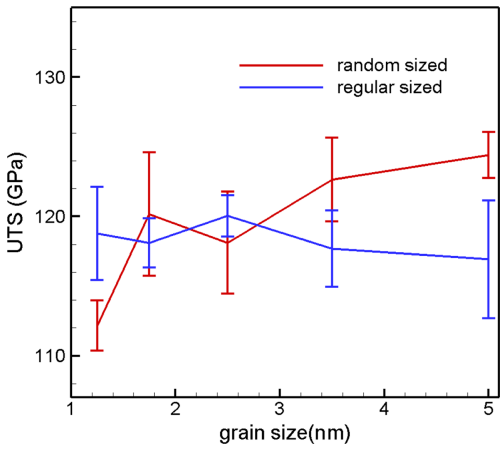

Fig. 7. UTS vs. grain size of polycrystalline graphene with random sized grains and with regular sized grains.

crack paths become more complicated, unless they propagate into the inside of the grains. This may explain the increasing behavior of UTS in this case.

4. Conclusions

In this study, we have investigated the effect of grain size distribution on the mechanical properties of polycrystalline graphene. We calculated the Young's modulus, fracture strain and UTS for models with random sized grains and with regular sized grains. As the grain size increases, Young's modulus increases, as expected. Therefore, there is no dependence of grain size distribution for Young's modulus. However, there is grain size distribution dependence for other quantities. The effect of the grain size on the fracture strain is differently determined for the two cases: the fracture strain of the regular sized grains shows higher correlation with the grain size than does that of the random sized grains. Furthermore, the grain size behaviors of UTS are also different for the two cases: the regular sized grains show the Hall-Petch effect but the random sized grains show the reverse Hall-Petch effect. We suggest that the difference may come from crack paths, which are differently generated for the different grain size distributions.

Acknowledgments

The authors acknowledge the financial support of the International Cooperative R&D program of the Ministry of Trade, Industry and Energy (MOTIE) of Korea (grant number: N0001711).

REFERENCES

1. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. B. T. Nguyen, and R. S. Ruoff, "Graphene-Based Composite Materials," *Nature,* **442** 282-86 (2006).
2. J. W. Jiang, J. S. Wang, and B. Li, "Young's Modulus of Graphene: A Molecular Dynamics Study," *Phys. Rev. B,* **80** 113405 (2009).
3. F. Liu, P. Ming, and J. Li, "Ab Initio Calculation of Ideal Strength and Phonon Instability of Graphene under Tension," *Phys. Rev. B,* **76** 064120 (2007).
4. Z. Song, V. I. Artyukhov, B. I. Yakobson, and Z. Xu, "Pseudo Hall-Petch Strength Reduction in Polycrystalline Graphene," *Nano Lett*., **13** [4] 1829-33 (2013).
5. Z. D. Sha, S. S. Quek, Q. X. Pei, Z. S. Liu, T. J. Wang, V. B. Shenoy, and Y. W. Zhang, "Inverse Pseudo Hall-Petch Relation in Polycrystalline Graphene," *Sci. Rep.,* **4** 5991 (2014).
6. B. Mortazavi and G. Cuniberti, "Atomistic Modeling of Mechanical Properties of Polycrystalline Graphene," *Nanotechnol.,* **25** [21] 215704 (2014).
7. J. Kotakoski and J. C. Meyer, "Mechanical Properties of Polycrystalline Graphene based on a Realistic Atomistic Model," *Phys. Rev. B*, **85** 195447 (2012).
8. Y. Park, S. Hyun, and M. Chun, "Grain Size Effect of Mechanical Properties of Polycrystalline Graphene," *Compos. Res.,* **29** 375-78 (2016).
9. S. Plimpton, "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *J. Comp. Phys*., **117** [1] 1-19 (1995).