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Coupled Effects of Temperature and Defects on the Mechanical Properties of 8-16-4 Graphyne: Atomistic Aspect

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***Abstract*— The 8-16-4 graphyne is a freshly discovered two-dimensional carbon allotrope that exhibits unique mechanical, electrical, and adsorption properties, with potential applications in single-atom catalysis, hydrogen storage, and flexible electronic devices. This research aims to deepen our understanding of the fracture behavior and mechanical characteristics of 8-16-4 graphyne monolayers. Through molecular dynamics simulations, we investigated how temperature, along with the interactions between temperature, vacancy defects, and microcracks, influences its mechanical performance. The results indicate that 8-16-4 graphyne fractures by the cleavage of ethylene bonds at a critical strain of approximately 0.29. The mechanical properties are significantly influenced by temperature, vacancy concentration, and microcrack presence. Compared to its sibling carbon allotropes, 8-16-4 graphyne shows reduced sensitivity to vacancy defects. Pre-existing microcracks alter its fracture modes.**

Keywords—8-16-4 graphyne; mechanical properties; molecular dynamics; vacancy defect; microcrack

I. INTRODUCTION

Graphyne is a two-dimensional carbon structure with sp-sp^2 hybridization, where the introduction of acetylene bonds increases the variety of graphene allotropes [1]. These different two-dimensional structures often exhibit distinct thermal, optical, and electrical properties, as well as tunable mechanical performance, allowing for the design and synthesis of materials tailored to specific needs [2].

Bandyopadhyay *et al.* predicted the 8-16-4 graphyne crystal structure using first-principles calculations and demonstrated its mechanical and thermal stability, introducing a new form of graphyne [3]. Tromer *et al.* further investigated its melting point, electrical conductivity, and the effect of strain on its band gap, finding that its band structure remains unchanged under moderate strain [4]. This unique electrical property positions 8-16-4 graphyne as a promising substrate material for flexible electronic devices. Jafari *et al.* investigated the adsorption behavior of 3d transition metals on 8-16-4 graphyne, suggesting that it could be an ideal single-atom catalyst with potential applications in hydrogen storage and carbon dioxide capture [5].

A deeper understanding of the mechanical properties of materials aids in further exploring their applications in various fields. This study investigates the mechanical properties of 8-16-4 graphyne under different environments through molecular dynamics (MD) uniaxial tensile tests. The study examines the coupled effects of temperature, vacancy defects, and microcracks on its Young's modulus, fracture strain, failure strength, and toughness. Additionally, the deformation and fracture mechanisms under different conditions are discussed.

II. MATERIALS AND METHODS

Figure 1 shows the crystal structure of an 8-16-4 graphyne monolayer, which has a lattice constant of approximately 7.36 Å and is composed of 8-membered and 16-membered carbon rings. First-principles calculations have demonstrated its dynamic and thermal stability. To explore its mechanical properties, uniaxial tension simulations were carried out using LAMMPS, employing the adaptive intermolecular reactive bond order potential (AIREBO-M) due to its accuracy in

modeling bond formation and breakage during fracture processes [6]. The MD simulations used square-shaped models. Periodic boundary conditions were applied in the two in-plane directions of the two-dimensional material to approximate an infinite system. Fixed boundaries were applied out-of-plane, with a 50 Å vacuum layer added to prevent periodic interactions in that direction. Convergence tests across six simulation systems, ranging from 1440 to 19600 atoms, indicated that system size has little effect on defect-free results. Thus, a 3600-atom system was selected for defect-free calculations.

Initially, an 8-16-4 graphyne unit cell model was constructed in ATOMSK based on its coordinates. The structure was then optimized using the conjugate gradient method to find the lowest energy stable configuration. The resulting lattice constant was found to be very close to the predicted value from DFT calculations, demonstrating the reliability of the simulations. To prevent excessive out-of-plane wrinkles from affecting the stability of the test, only in-plane initial velocities were assigned to the atoms during velocity initialization, allowing the system to reach its target temperature. Subsequently, the material was equilibrated for up to 4 ps under the NPT ensemble to remove internal stresses and obtain a dynamically stable initial configuration at finite temperature. Based on convergence tests, the tensile strain rate was set to 1×109/s to balance accuracy and computational time. At a constant strain rate, the box length in the tensile direction is increased at each time step, while atomic coordinates are remapped, and the stress in the other directions is kept at zero to simulate a uniaxial tensile test. When calculating stress, the thickness of the carbon atom layer was assumed to be 3.34 Å, a standard effective thickness for 2D carbon materials. Collect the stress-strain data at each integration time step, and compute the average every 250 steps to plot a smooth stress-strain curve. Use OVITO to visualize the atomic coordinate data.

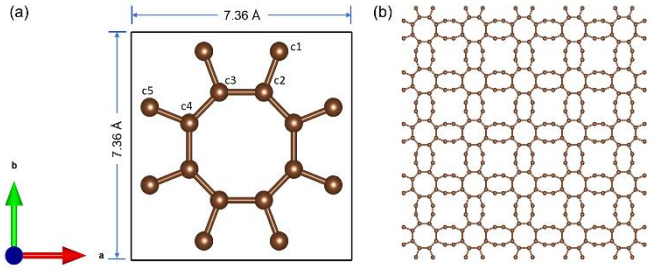


Fig. 1. Schematic diagram of the 8-16-4 graphyne structure. (a) Single-cell structure, (b) a monolayer of pristine graphyne was produced by VESTA. The letters "a" and "b" in the bottom-left corner represent the orientation of the coordinate system.

III. Results and Discussions

A. Temperature Effect

Temperature plays a crucial role in determining the mechanical properties of materials, especially for the use of two-dimensional materials in extreme conditions. This may be attributed to the ability of the 8-membered rings in 8-16-4 graphyne to undergo greater structural deformation before bond breaking. Temperature decreases the mechanical properties of graphyne in a non-linear manner. As the temperature increases to 900K, the Young's modulus and fracture strength decrease by 7% and 41% compared to those at 300K. In contrast, graphene's temperature dependence is linear [7]. Figure 2d visually represents the extent of the temperature's impact on four key mechanical performance parameters in terms of percentage variance. Temperature significantly affects the large deformation region and the critical failure conditions, while its influence on the Young's modulus during the elastic deformation stage is minimal.

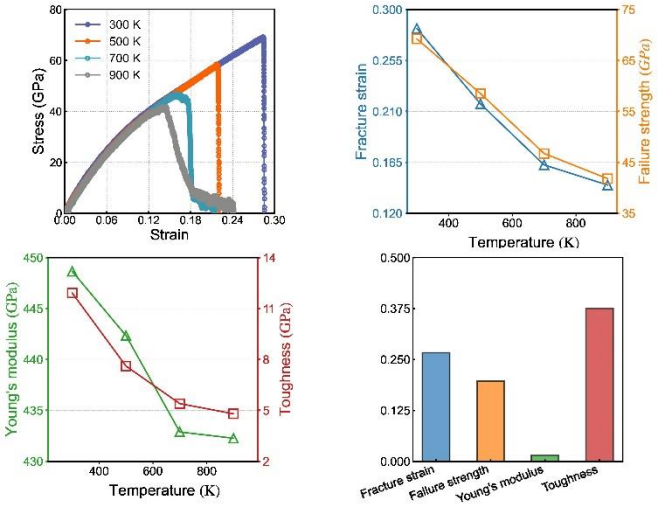
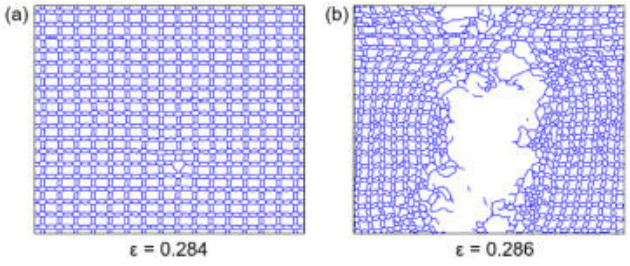


Fig.2 . Tensile test results at different temperatures. (a) Stress-strain curves; (b, c) Relationship between temperature and four key mechanical properties; (d) Percentage variance of the four key mechanical properties.

Furthermore, temperature affects the fracture mechanism of 8-16-4 graphyne. As shown in Figure 2a, at 700K, after the stress reaches its maximum value, it no longer rapidly drops to zero but instead shows a phase resembling plastic failure, which is even more pronounced at 900K. Further analysis of atomic trajectories reveals that this behavior may be related to structural transformations. As shown in Figure 3, at low temperatures, the breaking of ethylene bonds causes cracks to propagate rapidly perpendicular to the tensile direction, leading to complete separation of the two parts. At high temperatures, the structure does not fully dissociate after damage, forming numerous one-dimensional carbon structures between the two parts. This structure is known as carbyne, which Zhu et al [8]. discovered through MD simulations to be influenced by the size of carbon rings and temperature, which are key factors in determining whether two-dimensional carbon structures will form carbyne under large strain. Additionally, in Figures 3c-d, carbon ring structures different from the original 8-membered and 16-membered rings can also be observed. The formation of carbon chains and localized structural phase transformations are the reasons for the material exhibiting some degree of plasticity at high temperatures.



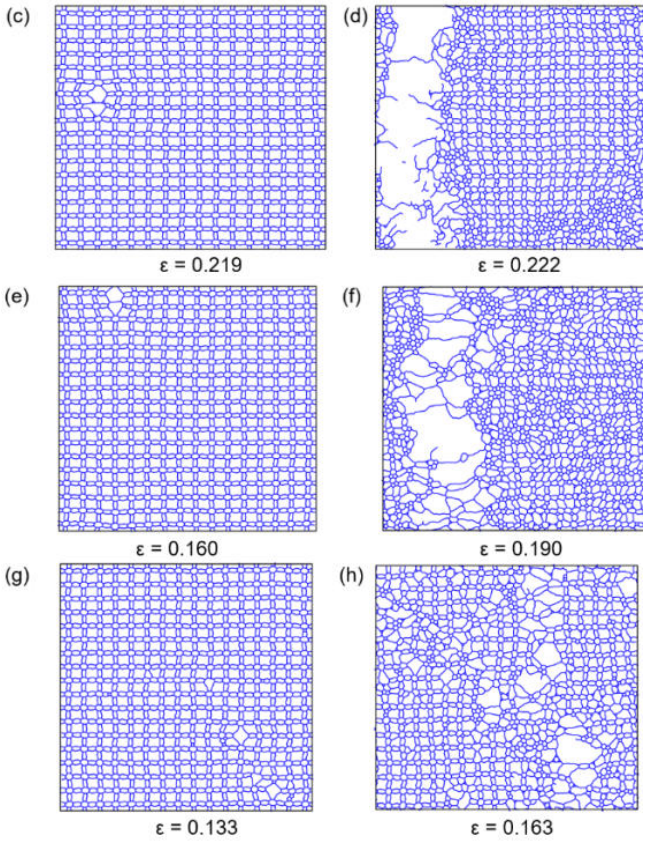


Fig. 3. Atomic trajectory images of tensile failure at different temperatures, showing the structure at the first bond breakage and significant defect propagation. (a, b) 300 K. (c, d) 500 K. (e, f) 700 K. (g, h) 900 K.

B. *The Vacancy-Defect Effect*

Vacancy defects are a common form of point defects, frequently observed in two-dimensional materials. These defects are often used to regulate the thermal and electrical properties of materials, and they also have a significant impact on the mechanical properties. Therefore, it is necessary to understand the impact of vacancy defects on the mechanical properties of 8-16-4 graphyne. This chapter first calculates the vacancy formation energies of 8-16-4 graphyne, followed by uniaxial tensile tests on systems with different concentrations of vacancy defects.

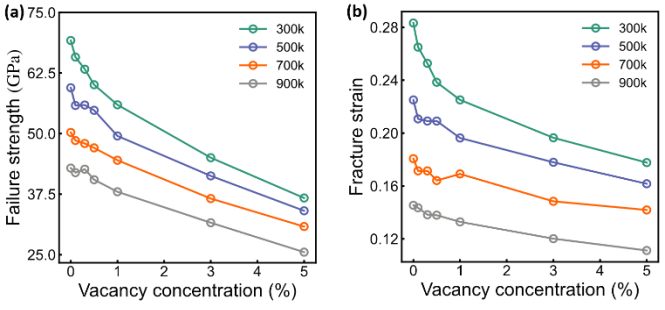


Fig. 4. Tensile test results for models with different concentrations of vacancy defects at 300K-900K. (a) Effect of vacancy defect concentration and temperature on fracture strain. (b) Effect of vacancy defect concentration and temperature on failure strength.

There are two inequivalent carbon atom sites in 8-16-4 graphyne (C1 and C2 in Figure 1), which are sp and sp2 hybridized, respectively. The vacancy formation energies for these sites are 2.798 eV and 6.254 eV, respectively, indicating that vacancy defects are more likely to form at the sp hybridized sites in 8-16-4 graphyne. The fracture strain and failure strength of the material decrease as the number of vacancies increases. A 1% vacancy defect reduces the failure strength of graphene by 31% [9], whereas the failure strength of 8-16-4 graphyne with the same defect density decreases by 19% compared to the pristine material. Vacancy defects in 8-16-4 graphyne disrupt the eight-membered rings and generate some short free carbon chains. Under tensile stress and thermal vibrations, the terminal atoms of these carbon chains may randomly form bonds with other sp-hybridized carbon atoms, leading to the creation of new carbon rings, which can compensate for the mechanical property losses caused by the defects.

At 300K, even a small number of vacancy defects can significantly impact the mechanical properties of the material. As the defect density increases, the additional weakening effect becomes relatively less pronounced. When the temperature rises from 300K to 900K, the failure strain of a system with a 1% vacancy defect density decreases by 19.2%, 16.7%, 11.4%, and 11.4%, respectively, compared to the perfect material. The fracture stress decreases by 20.5%, 12.8%, 6.4%, and 7.4%, respectively. This could be due to the increased atomic vibrations at higher temperatures, which enhance the likelihood of dangling atoms bonding with other atoms during stretching.

C. *Cracks and Fracture Toughness*

In addition to vacancies, real materials also contain other defects such as dislocations and microcracks. Microcracks can cause stress to concentrate locally within the material, which can further lead to fracture, often significantly affecting the material's ultimate stress and strain. This chapter studies the impact of crack length and temperature on the mechanical properties of 8-16-4 graphyne.

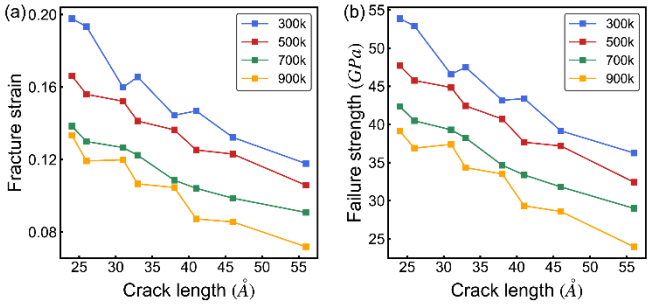


Fig. 5. Tensile test results for models with different crack lengths at 300K-900K. (a) Effect of crack length and temperature on fracture strain. (b) Effect of crack length and temperature on failure strength.

As shown in the results of Figure 5, both the increase in crack length and the increase in temperature lead to a decrease in the fracture strain and failure strength of 8-16-4 graphyne. In the crack systems created, there are two different atomic bonding configurations at the crack tip, as shown in Figure 6. The different crack tips produce different critical stresses for crack propagation, which causes the fluctuation in the decline of the material's mechanical properties with increasing crack

length in Figure 5.

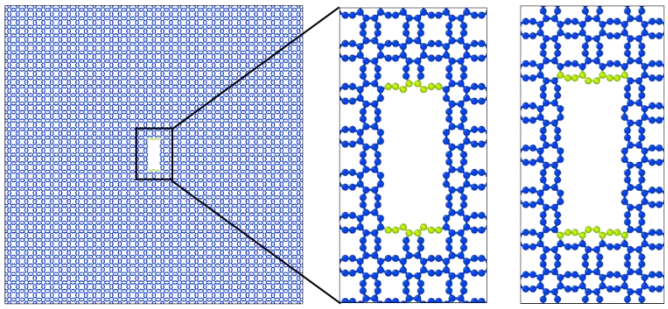


Fig. 6. Tensile test results for models with different crack lengths at 300K-900K. (a) Effect of crack length and temperature on fracture strain. (b) Effect of crack length and temperature on failure strength.

When tension is applied along the x-axis, the chemical bonds aligned with this axis endure more stress than those oriented perpendicularly. This phenomenon is associated with the cross-like architecture of 8-16-4 graphyne. Given that double bonds are weaker than triple bonds, the ethylene bonds along the x-axis are the first to break during deformation, initiating the formation of cracks. In the absence of defects, the fracture typically begins with the breaking of the C2-C3 ethylene bond, which leads to the disintegration of the octagonal structures and causes cracks to propagate along the y-axis. Whether defects are present or not, at 500K and below, defect propagation occurs rapidly. At 500K, cracks propagate perpendicular to the tensile direction at a speed of approximately 3 km/s, leading to the complete fracture of the material.

In defect-free model at elevated temperatures, the overall stress is reduced, making it less likely for localized bond breakages to develop into full cracks, with defects appearing in multiple regions of the model. However, microcracks in the model influence the fracture behavior of the material. Unlike defect-free and vacancy defect models, all models with microcracks exhibit brittle fracture at 700K and 900K. The weakening effect of microcracks on the mechanical properties of 8-16-4 graphyne is significantly greater than that of point defects. Initial defects formed at the tips of microcracks, which then rapidly propagated through the entire model. No Carbyne structures were formed during fracture, and the stress-strain curve no longer exhibited characteristics of plastic failure.

IV. Conclusions

In this work, MD simulations were used to perform uniaxial tensile tests on pristine and defect-containing 8-16-4 graphyne models at different temperatures. The coupled effects of defects and temperature on the failure stress and fracture strain under uniaxial stress were discussed, and the corresponding mechanisms were analyzed through atomic visualization. The results show that temperature affects the failure mode of 8-16-4 graphyne. At 300K, the material experiences brittle fracture at a strain of around 0.29, whereas at higher temperatures, the rate of defect propagation significantly decreases, and the formation of carbon chains and new carbon rings is observed. The mechanical properties of 8-16-4 graphyne exhibit a nonlinear downward trend with increasing temperature. Due to the presence of dangling carbon chains, the sensitivity of 8-16-4 graphyne to vacancy defects is lower compared to graphene, and this sensitivity is even less pronounced at high temperatures. Cracks have a more significant weakening effect on the mechanical properties of 8-16-4 graphyne than vacancy defects. Cracks may cause the failure mechanism at high temperatures to shift from ductile to brittle.

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