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SYNTHESIS OF TWO-DIMENSIONAL Fe-C ALLOY VIA MOLECULAR DYNAMICS SIMULATION

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ABSTRACT

Formation of two-dimensional (2D) Fe-C alloy with square lattice structure from the liquid state is studied via molecular dynamics (MD) simulation. The researchers find that the crystallization of 2D Fe-C alloy exhibits a first-order-like phase transition. Evolution of structural and thermodynamic properties upon cooling from the melt of the model is investigated in details. Structural properties of the $Fe_{50}C_{50}$ model are investigated via the radial distribution function (RDF), coordination number, interatomic distance, and bond-angle distributions. The researchers find that Fe-Fe distance is 2.62Å, which is close to the value of DFT calculations and experiments. In addition, various types of structural defects are studied such as vacancies of different shapes and rings of several sizes clearly using the visualization's software Visual Molecular Dynamics (VMD). Moreover, it can be proposed that the 2D Fe-C material would have many important applications in electronics and mechanic devices.

Keywords: molecular dynamics simulation, two-dimensional Fe-C, square lattice struture, phase transition.

1. Introduction

Finding a two-dimensional (2D) magnetic material has long been a concern of the scientific community. If this kind of material exists, it is possible to invent large data storage devices with very a small size and many other useful applications. The introduction of experimental graphene by Novoselov and co-workers can be seen as a pioneering step in the field of two-dimensional materials research (Novoselov, 2016). Over the past decade, the field of 2D materials has attracted many researches by both simulations and experiments. Many other 2D materials are also found which can have practical applications such as silicene, germanene, etc. (Tang, 1991; Hoang, 2014). However, for 2D materials found such as graphene or silicene, there is no band gap which can not be applied in semiconductor technology. To solve this problem, the 2D membrane of the various alloys is researched (Bekaroglu, 2010; Şahin, 2009; Lin, 2013; Koskinen, 2015; Yang, 2015).

J. Zhao and co-workers experimentally obtained 2D Fe material from the chemical vapor deposition (CVD) method (Zhao, 2014). With the MD simulation method, V.V.Hoang and co-workers obtained 2D Fe material from the liquid state (Hoang, 2017).

Their results indicate that the bond-length between atoms is about 2.45Å which is very close to 2.44Å and 2.41Å are found by calculating the DFT (Thomsen, 2015) .Y. Shao and colleagues conducted a 2D Fe-C alloy study of different Fe concentrations using ab initio particle swarm optimization technique (Zhao, 2014). However, to the best of our knowledge, the 2D Fe-C alloy membrane has not been studied clearly. Herein, the researchers have successfully simulated the two-dimensional structure of Fe-C alloy by using molecular dynamics (MD) simulation. The simulations suggest that 2D Fe-C alloy can be synthesized from the liquid state via using the 2NN MEAM potential. It opens the next research direction related to energetic stability, dynamic stability, thermal stability, mechanical stability, mechanical properties, electronic properties of 2D Fe-C material.

2. Calculation

The initial model containing 6400 randomly distributed atoms (3200 Fe and 3200 C atoms) is relaxed at 6000K for 10^6 MD steps in order to get an equilibrium 2D liquid state. Then the model is cooled from 6000 K to 300K at cooling rate of 10^{11} K.s^{-1}. The final configuration obtained at 300K is relaxed for 10^6 MD steps before analyzing structural characteristics. During the cooling process, periodic boundary conditions are applied for the x and z directions, whereas the elastic reflection boundary is applied for y ones.

The researchers used the Large-scale Atomic/ Molecular Massively Parallel Simulator (LAMMPS) software for MD simulation with the Verlet algorithm and MD time step is 01fs [13]. The ISAACS software is employed to calculate ring statistics. The VMD software are used for 2D visualization of atomic configurations (Humphrey, 1996).

The interaction between Fe, C atoms in the model is described via the 2NN Meam potential (Liyanage, 2014) .S.I.Liyanage and his colleagues have also improved the 2NN MEAM for the Fe-C alloy system for the purpose of predicting the structure and properties of cementite. This potential is thought to be good for the prediction of thermal properties, the elastic mass, the crystal lattice constants of Fe and C in the natural crystal structures that are consistent with the experiment (Liyanage, 2014). In the MEAM, the total energy of a system is approximated as found previously (Lee, 2000):

$$\mathrm{E} = \sum_{\mathrm{i}} \left[\frac{1}{2} \sum_{\mathrm{j}(\neq \mathrm{i})} \Phi\left(\mathrm{R}_{\mathrm{ij}}\right) + \sum_{\mathrm{i}} \mathrm{F}\left(\rho_{\mathrm{i}}\right) \right]. \quad (1)$$

F_i is the embedding function, $\overline{\rho_i}$ is the background electron density at site *i*, and $\Phi_{ij}(R_{ij})$ is the pair interaction between atoms *i* and *j* at a distance R_{ij}.

3. Results and discussions

3.1. Thermodynamics and evolution of structure upon cooling from the liquid state

The dependence of total energy per atom of the system on the temperature in a process indicates the change in the properties of the system relatively to the phase

transition. This is an important information that needs to be explored to understand crystallization. Temperature dependence of total energy per atom of the $Fe_{50}C_{50}$ model upon cooling from the liquid state can be seen in Figure 1. The graph of total energy change by temperature shows that initial energy decreases linearly by temperature, then at 3200K there is an abnormal change. Then, when the temperature reaches 2000K, the graph again represents the linear change of energy with temperature. Crystallization temperature can be considered as the middle point of this range, $T_X = (3200 + 2000)/2 = 2600K$. This point is rather higher than that found for the result of K. Belashchenko and co-workers for the bulk ($T_X = 2500K$, see Ref. (Belashchenko, 2011) .This can be explained by the fact that in 2D space, the thermal motion is limited in one direction.

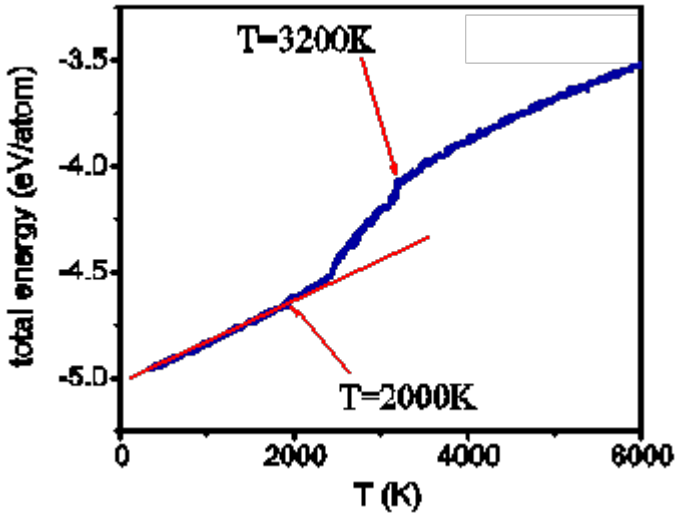


Figure 1. *Temperature dependence of total energy of $Fe_{50}C_{50}$*

In addition, the evolution of structure of the model upon cooling from 6000K to 300K can be seen in Figure 2. During cooling from 6000K, at 3300K it can be seen that the first peak is quite low, the RDF is smooth, almost without side vertex, representing the near-typical order of liquidity. At the 3200K, the first sub peak-appears to be quite apparent, starting with a change in the structure of the model, beginning of the phase transition. The lines were almost unchanged until 2600K, with the extra vertices appearing more clearly along with the peak height one and the double peak increasing indicating a significant increase of the crystal structure. As the temperature goes down, the height of the vertices increases and becomes more pronounced. At 2300K and 2000K, there is no significant difference in the extra vertices, indicating that the model is almost completely crystallized. At room temperature, the RDF curve is clearly different in height and boldness indicating that the model is completely crystallized at this temperature.

More details of evolution of structure of models upon cooling from the liquid state can be seen via mean coordination number distributions in Figure 3. Cut off radii (R_c) for the Fe-C, Fe-Fe, C-C links are respectively equaled to 2.7Å, 3.25Å and 3.2Å (corresponding to the first minimum position after the first peak of the radial distribution function). At high temperatures, the mean coordination number (CN) is relatively small demonstrating that the atoms are oscillating and far apart. The mean CN of the system has a tendency to increase with decreasing temperature and stabilizing after 2600K. This is a behavior of phase transition at this temperature. At low temperatures, the mean CN is almost constant, approximately equal to 4. This proves that the model approaches crystallization. With this result, proving that the model obtained is in the form of a square lattice structure. For the square lattice structure, the coordination number is the same for all atoms in the system (Z = 4).

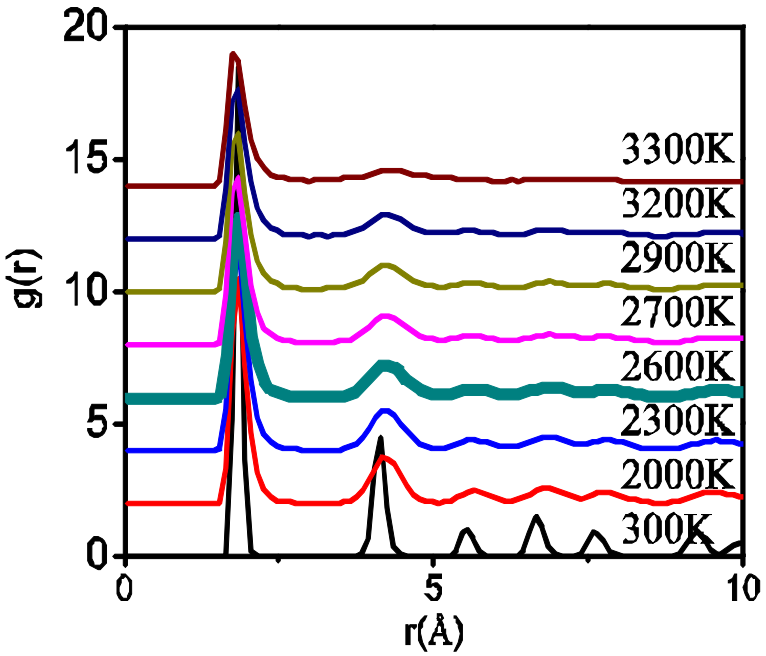


Figure 2. *Evolution of RDF of model obtained upon cooling from the liquid state (Fe-C)*

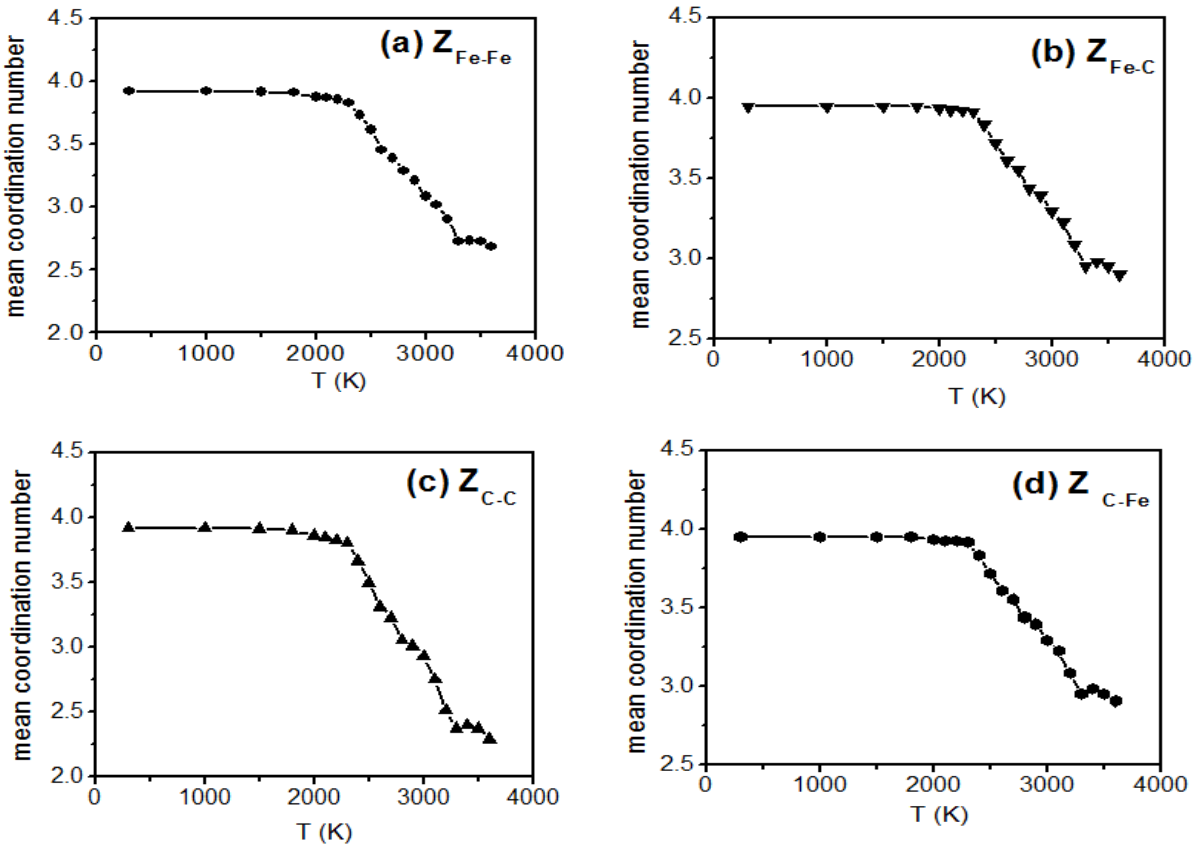


Figure 3. *Temperature dependence of mean coordination number*

To understand this mechanism more clearly, VMD software was used to visualize the phase transition. In particular, the intersection of links shows the position of the atoms in the model. Visualization of the model according to the temperatures from 2600K to 300K is shown in Figure 4.

At the temperature of 2600K, the model began to appear crystallization. At $T = 2000K$, the defects are gradually formed clearly. Finally, at $T = 300K$ (the fully crystallized model) the topology is clearly shaped and create a pretty square grid.

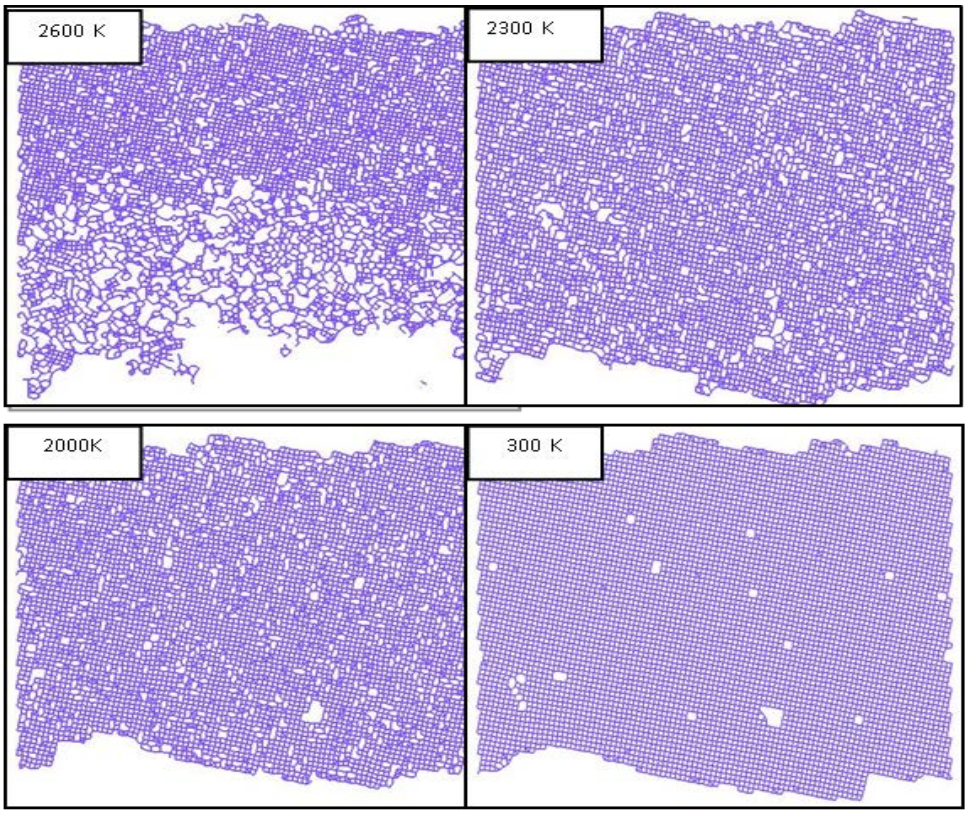


Figure 4. *Visualization of the model according to the temperatures from 2600K to 300K*

3.2. Structure of the Fe-C model obtained at 300K

Details of the structure of 2D Fe-C material obtained at 300K by cooling from the liquid state can be seen in Figures 5,6,7, and 8. The model is relaxed for 10^6 MD steps, then it is used to calculate the interatomic distance distributions, see Figure 5. The peak with the highest concentration of the Fe-Fe bond is around 2.62Å which is close to with the Y.Shao's calculation (2.65Å) (Zhao, 2014). Whereas the distance between two types of pairs of C-C, Fe-C at about 2.62Å, 1.84Å.

It can be found that the fraction of the coordination number Z=4 is high, indicating a nearly perfect crystalline square structure (Figure 6). Similarly, it can be found that 95,8% of the rings are 4-fold. In addition, the researchers find the existence of small or large membered rings such as 3-fold, 5-fold, 6-fold, and 8-fold rings, their fraction is very small (see the Figure 7).

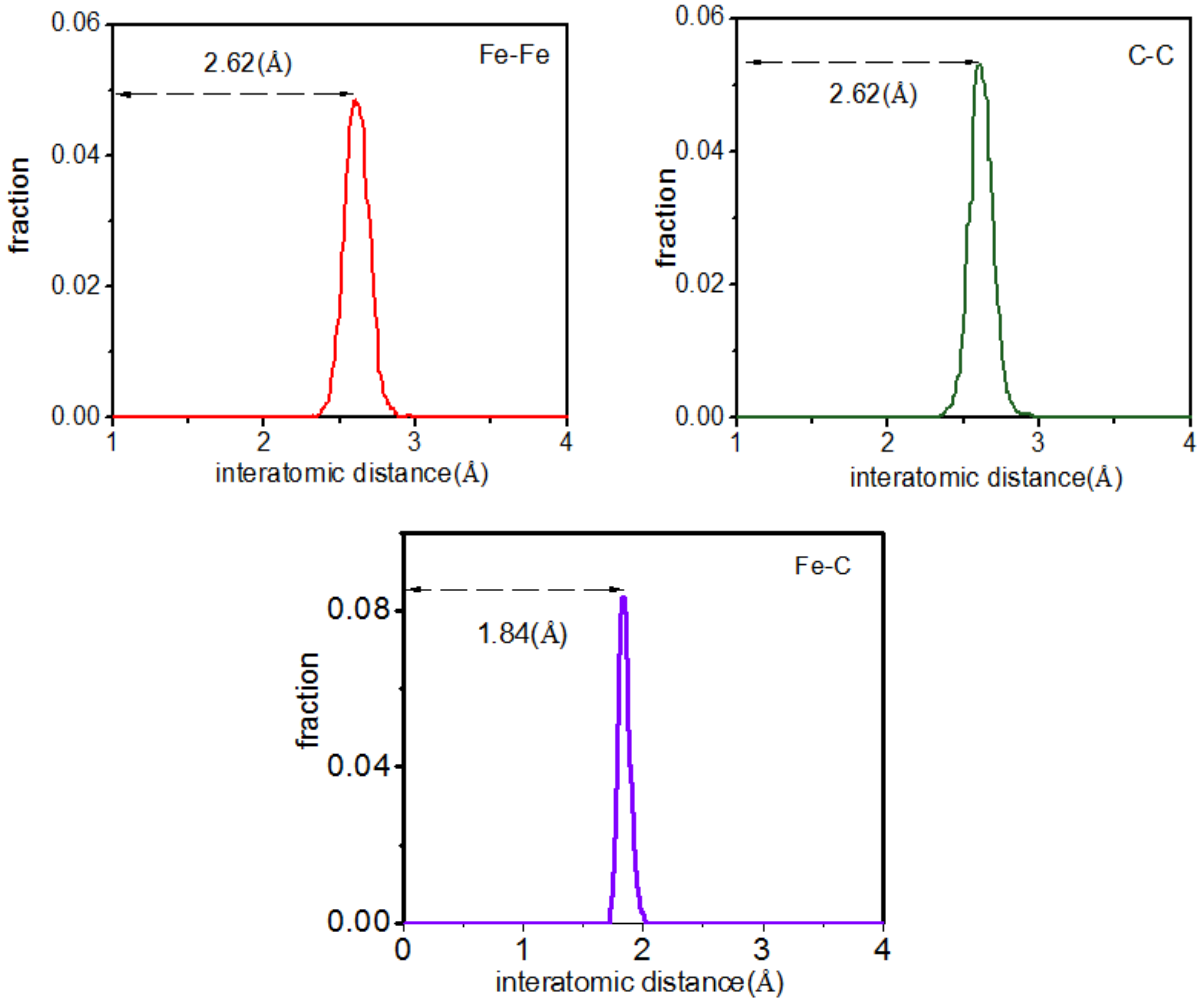
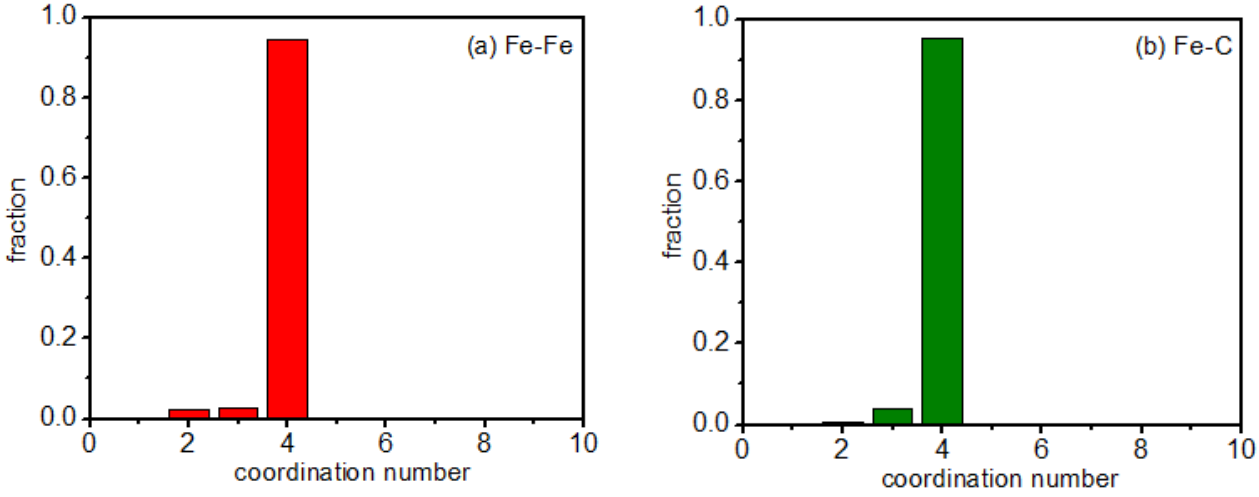


Figure 5. *Interatomic distance distributinons in the model*



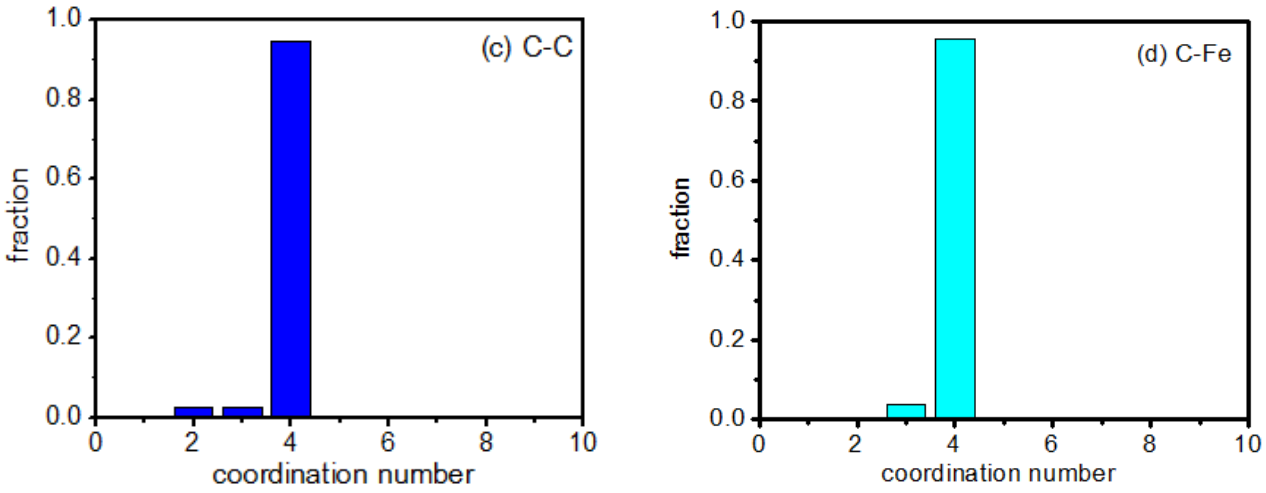


Figure 6. *Coordination number distributions in the model*

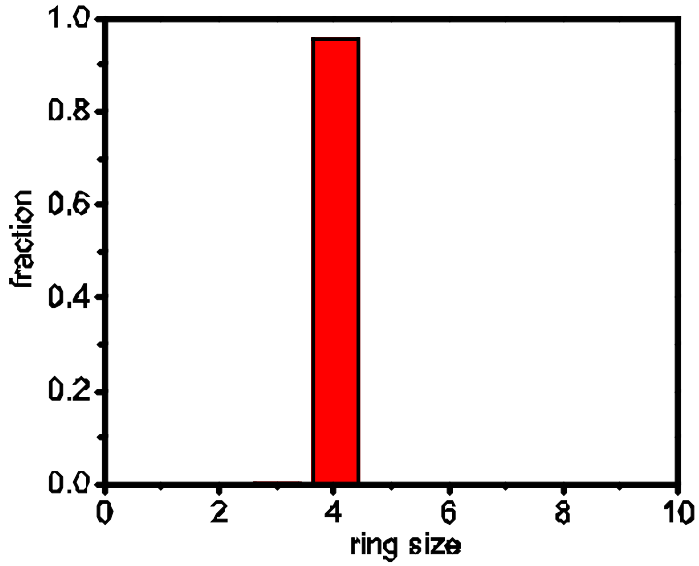


Figure 7. *Ring distributions in the model*

2D visualization of the atomic configuration of the Fe-C model obtained at 300K provides good insights into the structure of the material (Figure 8). It is clear that the atomic configuration exhibits a square structure. In addition, it can be seen that the received model is not perfect and contains a few defects. This may affect the physical properties of the material.

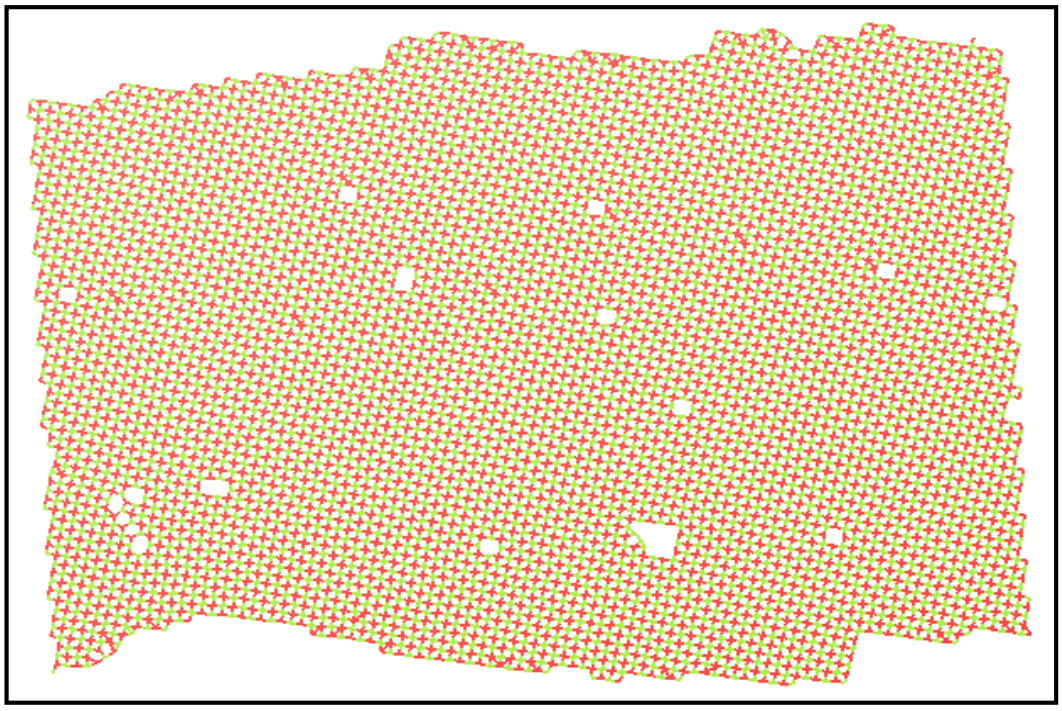


Figure 8. *2D visualization of atomic configuration of model obtained at 300K*

3.3. Some defects of structure of 2D Fe-C alloy

The model has a square structure, so many defects are similar to research of Prof. V.V. Hoang about a formation of 2D crystals with square lattice structure [18]. However, the defects are often created by the same causes related to the process of force interaction and thermal movement during the crystallization process.

The defects of the model are shown in Figure 9. Firstly, it can be seen that the model with double triangular defects created by a deformed square. The reason is that when the square structure is deformed, two a Fe-Fe atoms become closer and form a Fe-Fe bond. A new type of disability found is vacancy defect which is the loss of atoms. Beside, disability is a large vacancy which making near-atomic link structures easily deformed because the link balance is altered and forms triangles or pentagon. In addition, there are a lot of distorted squares showing an imperfect structure especially squares near the boundary.

With calculating by DFT, S. Haldar and co-workers show that magnetic properties can change in a positive direction by increasing vacancy (Haldar, 2014). Therefore, it is obvious that losing the C or Fe atoms should lead to affecting the magnetism of the Fe-C film.

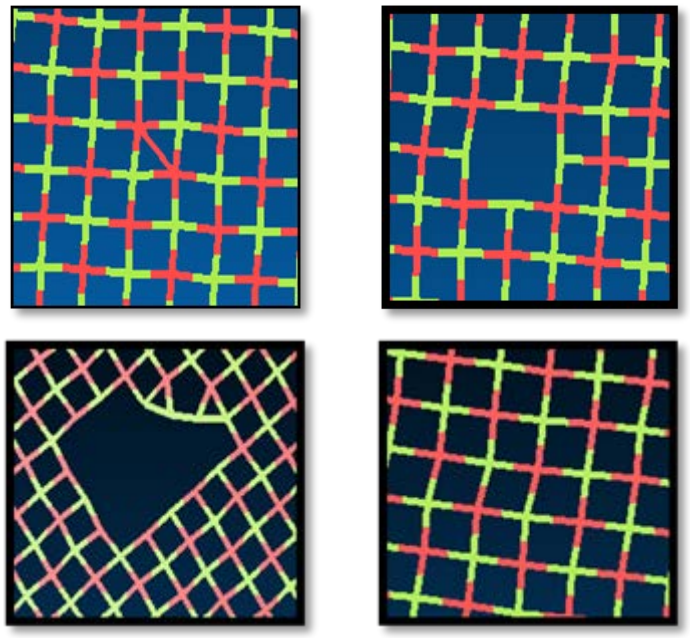


Figure 9. *Some defects of $Fe_{50}C_{50}$ model at 300K*

4. Conclusions

By using the molecular dynamics simulation, the researchers have successfully simulated a new two-dimensional Fe-C. The obtained results demonstrate the 2D Fe-C material can be flexibly produced from the liquid state. The freezing temperature of the two-dimensional iron carbide membrane from the liquid FeC-has a reasonable value and it is about 2600K. The final model obtained at 300K has the square structure, the Fe-Fe linkage constant is 2.62Å, the C-C is 2.62Å and the Fe-C is 1.84Å.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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TỔNG HỢP HỢP KIM 2 CHIỀU Fe-C BẰNG PHƯƠNG PHÁP ĐỘNG LỰC HỌC PHÂN TỬ

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TÓM TẮT

Sự hình thành hợp kim Fe-C hai chiều (2D) có cấu trúc lưới ô vuông từ trạng thái lỏng được nghiên cứu bằng phương pháp động lực học phân tử (MD). Chúng tôi tìm thấy sự tinh thể hóa hợp kim Fe-C hai chiều tuân theo chuyển pha loại 1. Sự thay đổi cấu trúc và tính chất nhiệt động học của quá trình làm lạnh từ trạng thái lỏng được nghiên cứu chi tiết. Tính chất cấu trúc của mô hình $Fe_{50}C_{50}$ được nghiên cứu thông qua hàm phân bố xuyên tâm (RDF),sự phân bố số phối vị, khoảng cách các nguyên tử và phân bố vòng. Chúng tôi tìm được khoảng cách Fe-Fe là 2.62Å, gần giá trị tính toán DFT và thực nghiệm. Ngoài ra, các loại khuyết tật cấu trúc cũng được tìm ra như nhiều hình dáng của các lỗ trống và các vòng có nhiều kích thước, thể hiện qua phần mềm VMD. Dựa vào các kết quả đạt được, chúng tôi đề xuất vật liệu Fe-C hai chiều sẽ có nhiều ứng dụng quan trọng trong các linh kiện điện tử.

Từ khóa: mô phỏng động lực học phân tử, màng 2 chiều Fe-C, cấu trúc ô vuông, chuyển pha.