

Molecular Dynamics Simulation of Reinforcing Steel Corrosion when Subjected to Both Chloride Attack and Mechanical Loading

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crossref <http://dx.doi.org/10.5755/j01.ms.26.3.20896>

Received 05 June 201X; accepted 27 January 2019

This paper describes the corrosion process of reinforcing steel under both chloride attack and mechanical loading. Molecular dynamics simulation is adopted to investigate the evolution process of passive film and oxidation process of reinforcement. The mean square displacement and self-diffusion coefficient of O₂ under different conditions are also obtained based on molecular dynamics simulation. It is shown that the present of chlorides can increase the energy of Fe atoms on the surface of Fe₃O₄ substrate, leading Fe atoms to separate from Fe₃O₄ easily and to get more chance to react with oxygen atoms. The interaction of chloride attack and mechanical loading can aggravate the damage of passive film on the surface of reinforcement and result in an increase of oxidation depth of Fe matrix. The coupled effects of chloride and static loading can accelerate the diffusion of O₂ to the iron matrix, thus increasing the oxidation reaction between the iron matrix and O₂.

Keywords: chloride attack, mechanical loading, reinforcement corrosion, molecular dynamics, passive film, oxidation process.

1. INTRODUCTION

The corrosion of reinforcing steel in concrete is one of the major causes of durability problems for reinforced concrete structures [1, 2]. It affects a large number of infrastructures, particularly those that are exposed to marine environments. In order to promote the effective application of reinforced concrete and ensure that the structure made from it has good performance during its service life, it is necessary to understand the mechanisms that how the reinforcement corrodes in a given environment condition and how its deterioration affects the performance of the structure.

Considerable research work has been carried out on the corrosion mechanism of reinforcement. Ji et al. described the process control of reinforcement corrosion in concrete and investigated the coupled effects of oxygen and corrosion products on the corrosion process of reinforcement in concrete structures [3, 4]. Stefanoni et al. measured local corrosion potentials, and the cathodic and anodic polarization curves on the reinforcement with different surface conditions by using "ec-pen" sensors [5]. Based on long-term durability tests, Sistonen et al. proposed three probable corrosion mechanisms of hot-dip galvanised reinforcement bar in cracked concrete [6]. Chitty et al. presented an analytical study on the long-term corrosion properties of ferrous reinforcement embedded in binders found in ancient buildings and investigated the morphological and physicochemical properties of corrosion products by using various modern methods of materials

testing such as optical and electronical microscopies, energy dispersive spectrometry coupled with scanning electron microscopy, mercury porosimetry, micro-Raman spectroscopy and micro-diffraction under synchrotron radiation [7].

Many researchers have investigated the influence of coupled chemo-mechanical process on the corrosion characteristics of reinforcement [2, 8]. Jaffer and Hansson investigated the composition and distribution of chloride-induced corrosion products of reinforcement in cracked-concrete with different loading conditions [9]. François and Ballim conducted the experiment on reinforced concrete elements under simultaneous loading and corrosion conditions [10, 11]. Their results showed that the load applied to a reinforced concrete beam plays an important role in the corrosion evolution of the reinforcement. Yu et al. discussed the corrosion initiation and propagation in pre-cracked reinforced concrete beams under a sustained loading condition while the beams were exposed to a chloride environment [12]. Jin et al. described the corrosive-cracking behavior of reinforced concrete members under both compressive loading and corrosive-ions attack [13].

Molecular dynamics (MD) simulation is a powerful tool that provides the real-time evolution of molecular structures and has been applied in many fields [14]; examples include the hydrogen embrittlement of metal [15], the performance of corrosion inhibitors used in concrete [16, 17], the transport properties of water in cement [18], and the moisture susceptibility of asphalt [19]. In MD simulation,

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atoms and molecules are allowed to interact for a period of time by approximations of known physics in order to explore the physicochemical properties of structures. With MD simulation, scientists are able to examine the motion of individual atoms and molecules in a way that would not be possible to get in laboratory experiments [20]. The existing studies mentioned above on the corrosion of reinforcement are mainly focused on the macro-scale analysis of corrosion characteristics of reinforcement under a combined chemo-mechanical process, such as the chloride attack and mechanical loading or the carbonation and mechanical loading. However, there are very limited studies in literature which were done by using the MD simulation to investigate the corrosion evolution of reinforcement under a combined chemo-mechanical attack.

The present paper is aimed to analyse the corrosion evolution of reinforcement under combined chloride attack and tensile loading in a micro-scale level. By using MD simulation, the micro molecular model of reinforcement corrosion is established. The ReaxFF reactive force field in Materials Studio software is adopted to investigate the combined chemo-mechanical effect on the damage of the passive film and oxidation process of reinforcement.

2. MOLECULAR DYNAMICS SIMULATION THEORY AND FORCE FIELD POTENTIALS

MD simulation is concerned with the description of the atomic and molecular interactions that govern the microscopic and macroscopic behaviors of physical systems. In MD simulation, the time dependent behavior of atomic and molecular system is calculated, giving a view of the dynamical evolution of the system. MD simulation is feasible to investigate the physicochemical properties of solutions and structures such as the interfacial phenomena and the dynamics of water molecules and ionic species in the solutions. In the most common version, the trajectories of atoms and molecules are determined numerically by solving Newton's equations of motion for a system of interacting particles, where the forces between the particles and their potential energies are calculated using interatomic potentials or force fields.

The ReaxFF reactive force field was established by Adri van Duin, which used a general relationship between bond distance and bond order and/or between bond order and bond energy, which leads to a proper dissociation of bonds to separate atoms [21]. Note that the traditional force field is not able to model chemical reactions because of the requirement of breaking and forming bonds; whereas the ReaxFF eschews the explicit bonds in favor of bond orders, which allows for continuous bond formation and/or bond breaking.

3. MOLECULAR DYNAMICS SIMULATION OF PASSIVE FILM EVOLUTION

The passive film of steel in concrete is formed in the alkaline environment provided by concrete pore solutions ($\text{pH} > 13$). The passive film is firmly adsorbed on the surface of reinforcement, which is very dense. Once the protective film around the reinforcement is broken, the active corrosion of the reinforcing steel occurs, which

causes the durability deterioration of reinforced concrete and could lead to catastrophic failure of the structure. For reinforced concrete structures exposed to marine environment the corrosion of steel is often caused due to chloride attack. In this section, the influence of different corrosion conditions on passive film evolution is to be investigated by using MD simulation, which can illustrate the failure mechanism of passive film on the reinforcement when subjected to combined chemo-mechanical attack in a micro-scale level. Three different corrosion conditions are to be considered herein. One is the reinforcement in a wet environment; one is the reinforcement in a wet environment with chloride attack; and one is the reinforcement in a wet environment not only with chloride attack but also with a mechanically tensile load.

3.1. Simulation details

3.1.1. Molecular modeling of Fe_3O_4

The passive film around the reinforcement is mainly composed of FeO , $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . The activation energies for the oxidation and reduction reactions between any two of the three oxides are relatively small. Therefore, these compounds can interchange generally with the pH value in concrete pore solution [22, 23]. For a concrete structure after having a long period of service, the pH value of its pore solution decreases with time, in which case the main component of the passive film transforms to Fe_3O_4 . Note that, Fe_3O_4 is known to be non-stoichiometric, which is likely to have defects that provides opportunity for chloride ions to penetrate into the oxide film [23]. In order to give a better description of the passive film around the reinforcement but without increasing extra computational efforts, in the present MD simulation the Fe_3O_4 is adopted as the passive film.

MD simulation is carried out by using Materials Studio software. A single Fe_3O_4 molecule is first constructed in the model. Then, 480 Fe_3O_4 molecules are generated by using the tool "Supercell". After conducting an energy minimization for the whole molecule system, the amorphous Fe_3O_4 structure is obtained by two annealing operations. The first annealing process is conducted by considering a canonical ensemble (NVT), in which the temperature reaches 900 K at a heating rate of 50 K/ps. The temperature is kept at 900 K for 10 ps and then decreases to 300 K at a cooling rate of 50 K/ps. The second annealing process is conducted by considering an isothermic-isobaric ensemble (NPT) with the same heating and cooling procedure used in the first annealing process. The molecular model of Fe_3O_4 after annealing is shown in Fig. 1.

3.1.2. Molecular modeling of liquid water

A H_2O molecule is established by using Materials Studio software. The bond length of H-O is 1.110 Å and the bond angle of H-O-H is 109.471°. The H_2O molecule is then optimized in a cubic box of side length 10 Å. After optimization, the bond length of H-O is 0.976 Å and the bond angle of H-O-H is 104.548°, which are nearly identical to the experimentally obtained values by Ashcroft [24]. Liquid water is simulated by considering a total of 500 H_2O molecules, which initially are randomly distributed in a cubic box. A water molecule system is then obtained by

using relaxation operation, as is shown in Fig. 2. The relaxation process is conducted by considering a canonical ensemble (NVT), in which the temperature is 300 K and the relaxation time is 2 ps. The structure size of obtained H₂O is 34.39 Å × 25.14 Å × 17.29 Å, the bond length of H-O is 0.951 Å and the bond angle of H-O-H is 104.292°.

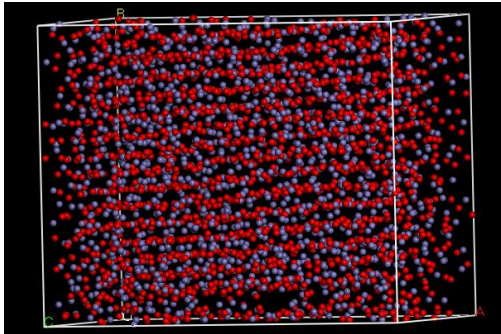


Fig. 1. Molecular modeling of Fe₃O₄ after annealing (Red balls are oxygen atoms and blue balls are iron atoms)

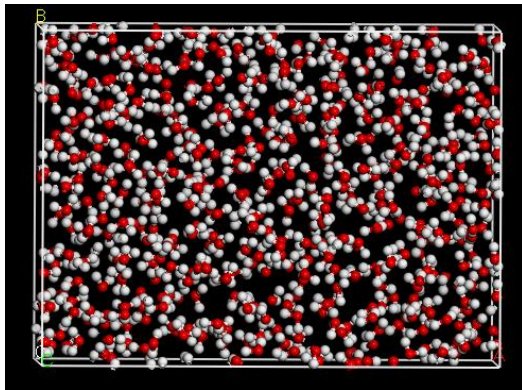
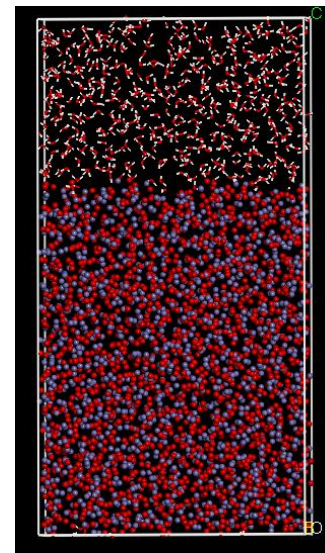


Fig. 2. Molecular modeling of H₂O (Red balls are oxygen atoms and white balls are hydrogen atoms).

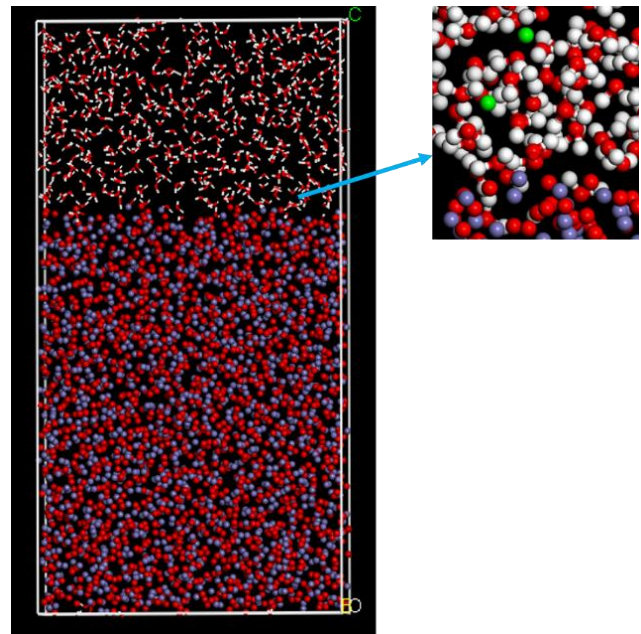
3.1.3. Molecular modeling of passive film with water and chloride ions

In the first case, the liquid water molecules (see Fig. 2) are located 2 Å above the amorphous Fe₃O₄ structure (see Fig. 1), which forms a system (denoted as H₂O + Fe₃O₄), as is shown in Fig. 3 a. In order to investigate the influence of chloride ions on the passive film evolution, the chloride solution is simulated by further adding 10 chloride ions into the water molecule system. As mentioned above, the chloride solution is located above the amorphous Fe₃O₄ structures to form a new system (denoted as Cl⁻ + H₂O + Fe₃O₄), as is shown in Fig. 3 b. By using a relaxation operation, the interface between water and passive film can be obtained. The relaxation process is conducted by considering a canonical ensemble (NVT), in which the temperature is 300 K and the relaxation time is 100 ps.

The structure size of obtained system is 34.39 Å × 25.14 Å × 66.88 Å, the bond length of H-O is 0.956 Å and the bond angle of H-O-H is 104.859°. With the application of tensile strain, the H₂O molecule can interact with Fe₃O₄ at the interface and the detailed discussion can be seen in section 3.2



a



b

Fig. 3. Initial configurations for passive film (Green balls are chloride ions): a–H₂O + Fe₃O₄; b–Cl⁻ + H₂O + Fe₃O₄

3.1.4. The application of uniaxial tension

In order to investigate the passive film evolution under the action of a combined chloride attack and mechanical loading, periodic boundary conditions are applied along x-axis direction for the passive film model constructed in section 3.1.3. The model is then subjected to a uniaxial tension which is conducted in the isothermal-isobaric (NPT) ensembles with the loading rate of 0.001/1 ns. The molecules on the left-hand side of the model are fixed and the strain is applied to the right-hand side of the model to obtain the deformations desired in the analysis step. The entire tension and reaction process are carried out at a constant temperature of 300 K and a constant pressure (one atmosphere) using the GULP code as implemented in the Materials Studio program system. Reactive force field (ReaxFF) is employed in the simulation with a time step of

0.5 fs. After the tension process is completed, the molecules on the both sides of the model are fixed and the system is then relaxed in a canonical ensemble (NVT) for 1 ps.

3.2. Results and discussion

3.2.1. The evolution of passive film under chloride attack

In this section, the influence of chloride ions on the structural organisation of Fe_3O_4 is investigated by using the model constructed in Fig. 3. After the completion of computation, the snapshots of molecules in the interface between Fe_3O_4 and H_2O are shown in Fig. 4. It is observed from the figure that there exist significant structural differences between the two corrosion conditions. When there is no chloride ion in the system, no obvious change exists in the structure of Fe_3O_4 . However, compared to the interface shown in Fig. 4 a, the transformation of Fe_3O_4 structure shown in Fig. 4 b is obvious. When the water contains free chloride ions, water molecules are ionized into H^+ and OH^- . A large number of Fe atoms located on the top of Fe_3O_4 are combined with OH^- in the water. The surface of Fe_3O_4 substrate becomes irregular, which indicates that the present of chloride ions in the water can damage the structure of Fe_3O_4 . The results show that, the high activity of chloride ions can increase the energy of Fe atoms on the surface of Fe_3O_4 substrate, which makes the Fe atoms separate from Fe_3O_4 easily. These separated Fe atoms can generate $\text{Fe}(\text{OH})_2$ by further combining with OH^- in water. After the destruction of Fe_3O_4 surface structure, chloride ions are adsorbed onto the new surface layer of Fe_3O_4 ,

leading to new Fe atoms to be separated from Fe_3O_4 substrate. This process is equivalent to that the passive film on the reinforcement is gradually stripped by chloride ions until it disappears, leading to the loss of protection of reinforcement.

3.2.2. The evolution of passive films under combined action of chloride attack and mechanical loading

In this section, the combined effect of chloride attack and mechanical loading on the structural organization of Fe_3O_4 is investigated by using the model constructed in figure 3. As is described in section 2.1.4, the applied strain was 0.05, 0.1 and 0.2 respectively. After the completion of computation, the snapshots of molecules in the interface between Fe_3O_4 and H_2O are shown in Fig. 5. It can be seen from the figure that the applied static loading affects the evolution of Fe_3O_4 structure, leading to the cracking of passive film. The crack width is found to increase with increased loading. When the applied strain is less than 0.05, the combined effect of chloride attack and mechanical loading on the evolution of passive film is not so obvious. However, after the applied strain reaches 0.1, cracks appear obviously in the molecular structure, as is shown in figure 5(c). When the applied strain reaches 0.2, these cracks coalesce rapidly and the maximum crack width is about 3.566 Å, as is demonstrated in figure 5(d). Since some of hydrogen atoms and chloride ions can penetrate into the interior of Fe_3O_4 substrate through cracks, the bond energy between the atoms of Fe_3O_4 molecules reduces.

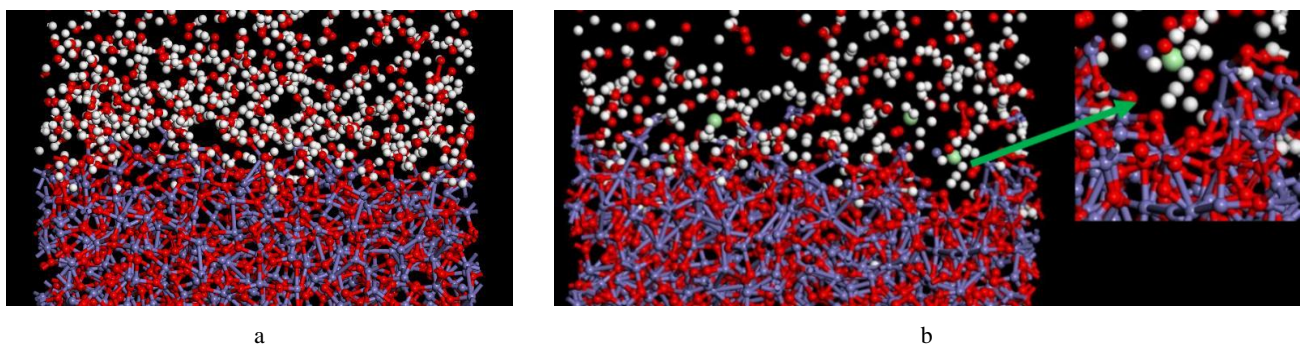


Fig. 4. Snapshots of molecules in the interface between Fe_3O_4 and H_2O under chloride attack (Green balls are chloride ions): a – without chloride ions; b – with chloride ions

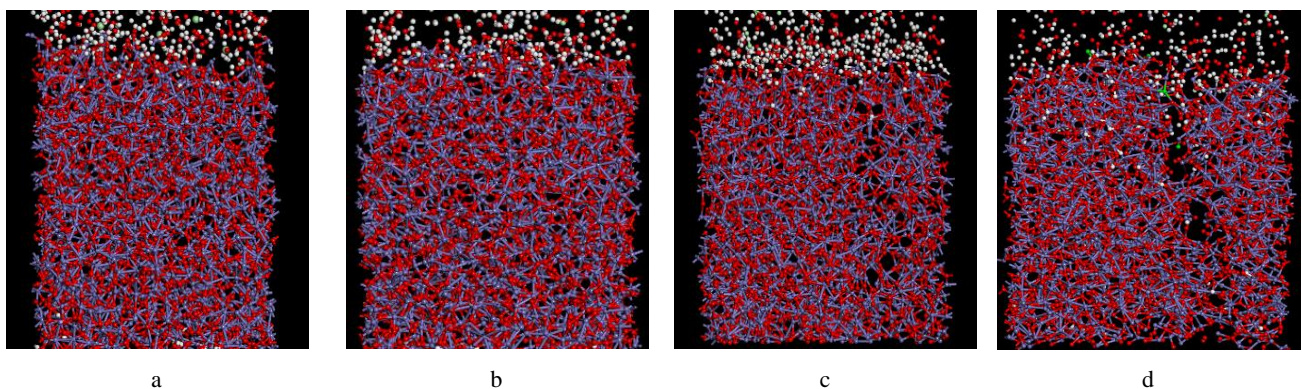


Fig. 5. Snapshots of molecules in the interface between Fe_3O_4 and H_2O under combined action of chloride and mechanical loading (Green balls are chloride ions): a – without loading; b – the applied strain is 0.05; c – the applied strain is 0.1; d – the applied strain is 0.2

Consequently, more hydrogen atoms can penetrate into the lower part of the Fe_3O_4 substrate, which can bond with Fe and O_2 atoms. This is equivalent to that the passive film on the reinforcement is further stripped. When the passive film on the reinforcement is broken, the corrosive items, like water, O_2 and Cl^- , could contact with the iron matrix, which makes the reinforcement more vulnerable to corrosion. Thus the combined action of chloride attack and mechanical loading can accelerate the corrosion of reinforcing steel.

4. MOLECULAR DYNAMICS SIMULATION OF OXIDATION PROCESS OFF REINFORCEMENT UNDER COMBINED CHLORIDE ATTACK AND MECHANICAL LOADING

Note that the corrosion of iron is an oxidation-reduction process, which destroys iron object and leaves it open to moist and/or air and results in the corrosion product, called rust. This chemical process combines iron and oxygen to form iron oxide. Given sufficient time, oxygen and water, any iron mass will eventually convert entirely to rust and the original iron will become a disintegrated rust product. In this section, the oxidation process of Fe atoms is investigated by using MD simulation. The corrosion conditions used in the simulation are the same as those described in section 2.

4.1. Simulation details

4.1.1. Molecular modeling of Fe matrix

A single Fe atom is generated by using Materials Studio software. After an optimization, the lattice constant of Fe is found to be about 2.857 \AA , which is consistent to the experimental result of Kittel (2.866 \AA) [25]. After then, 1531 Fe atoms are generated by using the tool "Supercell". The size of the constructed Fe matrix system is $28.85 \text{ \AA} \times 22.86 \text{ \AA} \times 22.86 \text{ \AA}$. After an energy minimization of the whole system, the structure of Fe matrix system is shown in Fig. 6.

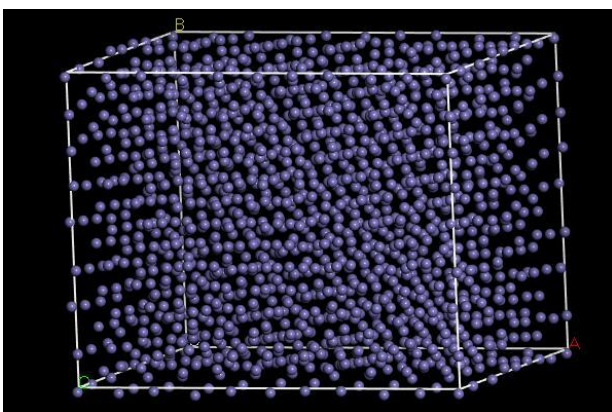


Fig. 6. Structure of Fe matrix system

In order to investigate the influence of mechanical loading on the oxidation process of reinforcement, periodic boundary conditions are applied along x-axis direction for the Fe matrix model constructed in figure 6. The loading and relaxation process are the same as those described in section 3.1.4. The applied strain is 0.05, 0.1 and 0.2, respectively.

4.1.2. Molecular modeling of O_2

Oxygen (O_2) molecule is established by using Materials Studio software, in which the bond length of O-O is 1.840 \AA . The O_2 molecule is optimized in a cubic box of side length of 10 \AA . The k-point set used in calculation defines the accuracy of the Brillouin zone sampling. In this study, the gamma point is chosen, which indicates that a single k-point at (0,0,0) is used for the density of state calculation. After an optimization, the bond length of O-O is found to be 1.245 \AA , which is consistent to the experimental result of Lide (1.210 \AA) [26]. A total of 200 O_2 molecules are randomly distributed in a space with the size of $28.85 \text{ \AA} \times 22.86 \text{ \AA} \times 136.35 \text{ \AA}$. In order to obtain better simulation results but without increasing extra computational efforts, the density of oxygen is set as 0.15 g/cm^3 , which is equivalent to the density of oxygen at ten atmospheric pressure. An O_2 molecule system is then obtained by using relaxation operation, as is shown in Fig. 7. The relaxation process is conducted by considering a canonical ensemble (NVT), in which the temperature is 300 K and the relaxation time is 2 ps.

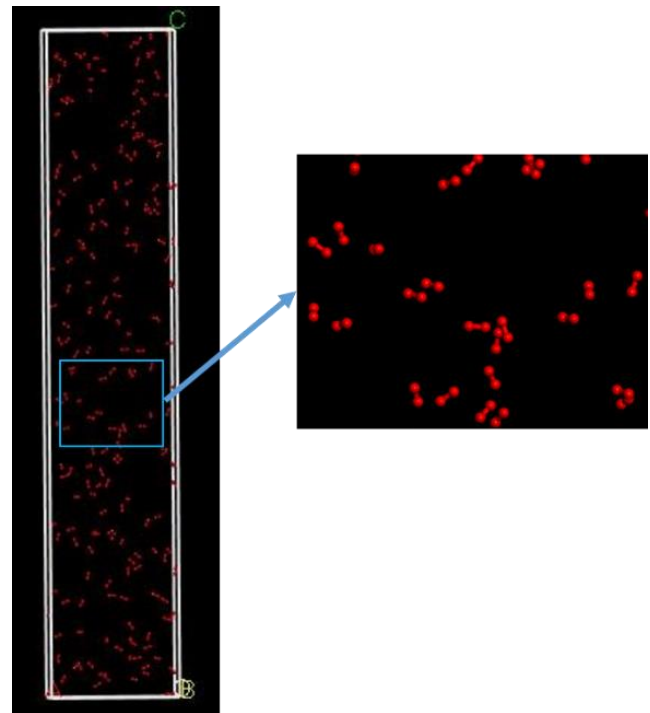


Fig. 7. Structure of O_2 molecules system

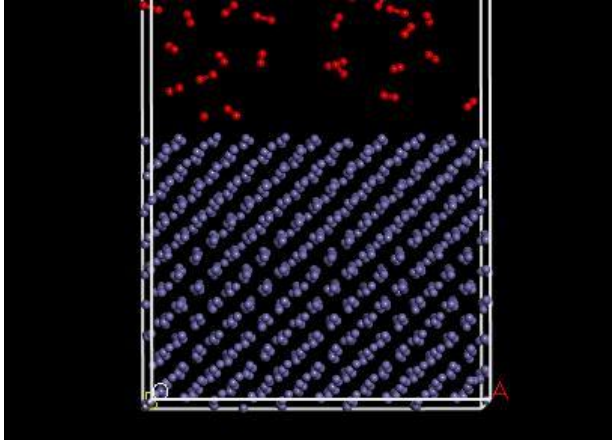
4.1.3. Molecular modeling of iron oxidation reaction

The generated oxygen molecules (see Fig. 7) are located 2 \AA above the Fe matrix (see Fig. 6), which forms a system, as is shown in Fig. 8 a. In order to investigate the influence of chloride ions on the oxidation process of Fe, ten chloride ions are added into the O_2 molecule system, which is located above the Fe matrix to form a new system, as is shown in Fig. 3 b. A total of five sets of models are established, as is listed in Table 1. The five systems are relaxed to generate realistic structure models. The relaxation process is conducted by considering a canonical ensemble (NVT), in which the temperature is 300 K and the relaxation time is 100 ps.

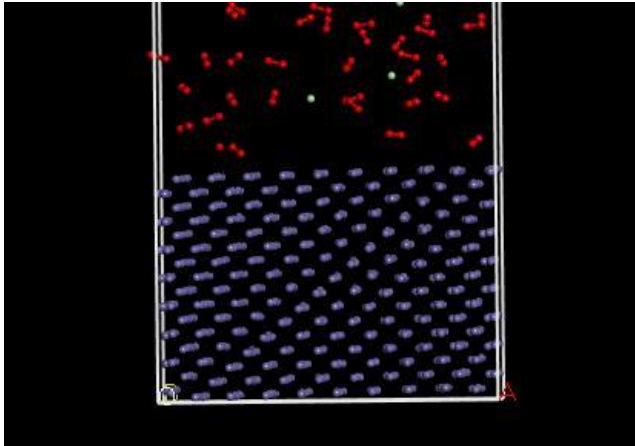
The oxidation process is conducted by using the GULP code as implemented in the Materials Studio software. The force field, time step and reaction temperature are taken to be the same as those described in section 2.1.4.

Table 1. The models employed for iron oxidation reaction

Model code	L0	L0-Cl	L5-Cl	L10-Cl	L20-Cl
Applied strain	0	0	0.05	0.1	0.2
Chloride	No	Yes	Yes	Yes	Yes



a



b

Fig. 8. Model construction process of iron oxidation reaction: a – without chloride ion; b – with chloride ion

4.2. Results and discussion

Fig. 9 shows the snapshots of the configuration of Fe oxidation reaction, which is based on the models

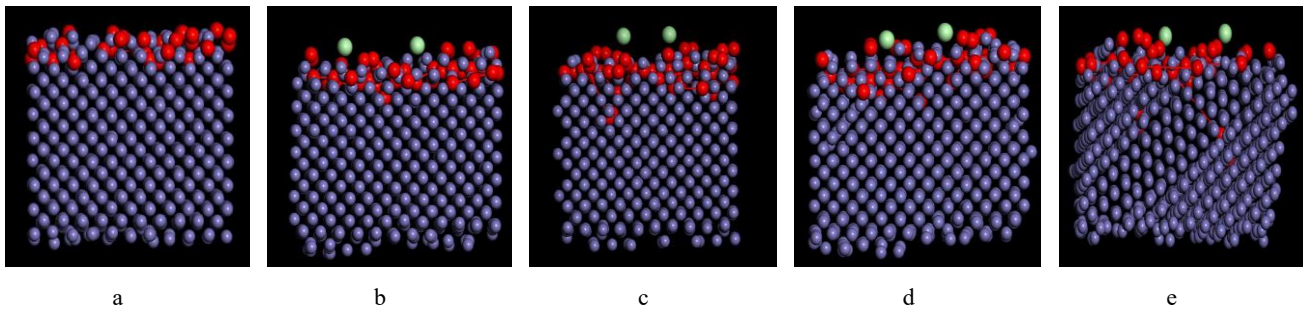


Fig. 9. Snapshots of the configuration of Fe oxidation reaction: a–L0; b–L0-Cl; c–L5-Cl; d–L10-Cl; e–L20-Cl

constructed in Table 1. The oxidation depths calculated for five individual systems are shown in Table 2. As is shown by the results obtained from model L0, a thin oxidation layer is formed on the surface of the Fe substrate, which indicates that the oxidation reaction can occur without the present of chlorides. The calculated oxidation depth is about 2.21 Å. However, under the attack of chloride ions, the oxidation depth of model L0-Cl is about 4.08 Å. Compared to model L0, it has an 85 % increase, which is very substantial. While under the combined action of chloride attack and mechanical loading, the oxidation depth is found to increase obviously with the increased mechanical loading. When the applied strain is 0.2, the oxidation depth is 10.88 Å. This, when compared to model L0-Cl, has an increase of 6.80 Å. Therefore, the combined action of chloride attack and mechanical loading has a significant influence on the oxidation process of reinforcement. This is attributed to the change of bond energy between atoms. The uniaxial tension leads an increase in the distance between Fe atoms, which reduces the ionic bonding between Fe atoms, and thus makes Fe atoms easier to combine with oxygen atoms. On the other hand, chloride ions can increase the adsorption energy of Fe-O, which facilitates the bonding between Fe and oxygen atoms. In summary, the combined action of chloride attack and mechanical loading can make the Fe matrix absorb more O₂ atoms and with the increased applied loading the oxidation depth increases, which promotes the oxidation reaction of Fe matrix. When there is sufficient oxygen, a thicker corrosion layer can be formed on the surface of reinforcement.

Table 2. The calculated oxidation depth

Model code	L0	L0-Cl	L5-Cl	L10-Cl	L20-Cl
Depth, Å	2.21	4.08	5.28	6.08	10.88

Mean square displacement (MSD) is a method to determine the displacement patterns of particles over time, which can help determine whether particles are free to spread and transport. In molecular dynamics simulation, MSD can be obtained directly from the particle position, as shown in Eq. 1.

$$MSD = \frac{1}{T - \Delta t} \int_0^{T - \Delta t} [r(t - \Delta t) - r(t)]^2 dt \quad (1)$$

$$= \langle [r(t - \Delta t) - r(t)]^2 \rangle$$

where T is the total simulation time, $r(t)$ is the location of atoms at the time of t .

The MSD evolution of O₂ under different conditions is shown in Fig. 10.

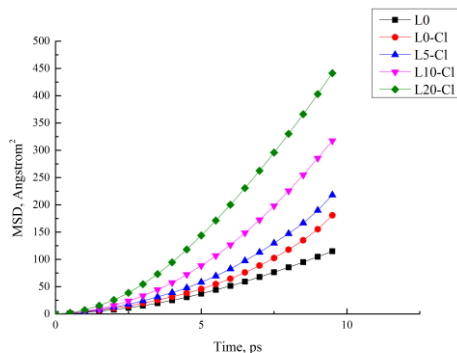


Fig. 10. The MSD evolution of O₂ under different conditions

According to Einstein's law of diffusion, the calculation method of self-diffusion coefficient in MD simulation is obtained as shown in Eq. 2.

$$D = \frac{1}{6} \lim_{\Delta t \rightarrow \infty} \frac{dMSD}{d\Delta t} \quad (2)$$

By linearly fitting the data in Fig. 10, the self-diffusion coefficient of O₂ under different conditions is obtained as shown in Fig. 11.

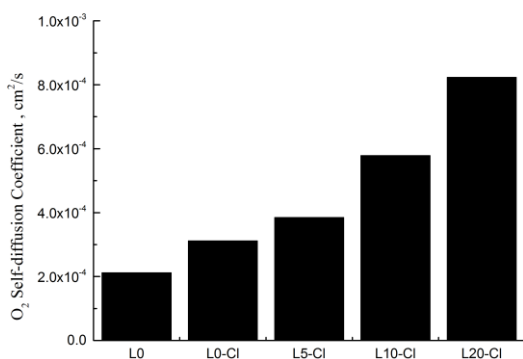


Fig. 11. The self-diffusion coefficient of O₂ under different conditions

It can be seen from Fig. 10 that the existence of chloride can increase the MSD of O₂. With the increase of static loading, the MSD of O₂ gradually increases.

It is indicated from Fig. 11 that, chloride can increase the self-diffusion coefficient of O₂ by 47.7 %, from 2.12 × 10⁻⁴ to 3.13 × 10⁻⁴. Besides, static loading can also increase the self-diffusion coefficient of O₂ by 163.3 %.

5. CONCLUSIONS

This paper presents an investigation of the corrosion process of reinforcement under the combined action of chloride attack and mechanical loading by using MD simulation. The evolution of passive film and the oxidation process of reinforcement are simulated using Materials Studio software and the corresponding reaction mechanism is discussed in detail. The results have demonstrated that the present of chloride ions in the water system makes the Fe atoms separate from Fe₃O₄ easier and quicker, which leads

to the passive film around reinforcement to be gradually stripped by chloride ions until it disappears. The oxidation depth of Fe matrix is found to increase substantially. The applied mechanical loading further affects the evolution of Fe₃O₄ structure, leading to the cracking of passive film. Owing to the combined action of chloride attack and static loading, the damage of passive film on the surface of reinforcement is aggravated. Especially when the applied strain reaches 0.2, these cracks coalesce rapidly and the maximum crack width of passive film reaches to about 3.566 Å. The oxidation depth of Fe matrix is found to increase noticeably with the increased mechanical loading. The oxidation depth of L20-Cl reaches to about 10.88 Å, which is 167 % of that of L0-Cl.

The existence of chloride increases the MSD and self-diffusion coefficient of O₂. Besides, the two parameters increases with static loading. It is indicated that the coupled effect of chloride and static loading accelerates the diffusion of O₂ to the Fe matrix, and further increasing the oxidation reaction between the Fe matrix and O₂.

Acknowledgments

The authors wish to acknowledge the financial support of "National Natural Science Foundation of China (Grant No. 51778577)" and "Natural Science Foundation of Ningbo (Grant No. 2018A610229)".

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