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Effects of Temperature and Flow on the Adsorption Behaviour of NaCl Solution on the Surface of MgO: A Molecular Dynamics Study

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Degradable magnesium alloy is one of the most promising scaffolding materials, which can provide a temporary opening into a narrowed arterial vessel and will progressively disappear thereafter. But its clinical application is not very extensive as it still has the problem of non-uniform degradation and rapid degradation rates, especially at the initial stage, which need further study to overcome. In this study, the adsorption properties of solution on the magnesium oxide, which is the first step of magnesium alloy reaction, is investigated by molecular dynamics simulation at different temperatures and flow velocities. The body fluid is simplified to NaCl solution. The number density of solution perpendicular to the MgO surface is calculated to analyse the adsorption capacity, the self-diffusion coefficient is researched to measure the adsorption rate. At same time, the effects of temperature and flow on the adsorption properties of solution are also clarified. The results show that there exist solution films at the surface of metal, and the solution can be divided into two zones: adsorption zone and free zone according to the density profile. As temperature increases, the adsorption rate of solution is improved while the adsorption capacity has little change. What’s more, it’s found that flow can accelerate adsorption, but decrease the amount of adsorption. This study improves the understanding of adsorption characteristics of NaCl solution from the microscopic point of view, which plays an important role in understanding the corrosion process of MgO.

1. Introduction

In recent years, the incidence of cardiovascular disease is getting higher and higher although people's living standards are improving. Interventional therapy is an effective treatment for coronary heart disease. Considering that the commonly used metal stent which exists in the blood vessel for life may lead to inflammation and the problem of restenosis is difficult to solve, the long term curative effect of metal stents is limited. Fortunately, the biodegradable stent provides the hope for solving this problem, and the most promising material is degradable magnesium alloy whose properties are close to natural bones and the degradation products can be absorbed (Esmaily et al., 2017). Degradable magnesium alloy can provide a temporary opening into a narrowed arterial vessel and will progressively disappear thereafter. In clinical, the ideal stent should meet the characteristics of slow degradation in the early stage and rapid degradation after the medical function is completed. The use of magnesium alloy is not extensive as it still has some defects needing further study to modify. In practical application, Mg-based biomaterials have rapid degradation rates in body fluids which would result in the loss of mechanical integrity (Li et al., 2014). And another key problem restricting the application of Mg-based biomaterials is the non-uniform degradation. The two problems are more notable at the initial stage. To clarify the degradation principle of magnesium alloy stent in body fluid, great efforts has been made by researchers. For example, some researchers did some studies on the element of the Mg alloy (Walker et al., 2012). Moreover, the influence of the component of the body blood on the corrosion was investigated in vivo experiment, such as the bovine serum albumin (Wagener et al., 2015), cells (Brooks et al., 2016) and ions in solution (Xin et al., 2010). Most of the solution used in the immersion tests was static (Zeng et al., 2015) and few studies had systematically researched the influence of flow on biodegradation of Mg and its alloy (Wang et al., 2014). Unfortunately, these studies have reported a large range of results due to the different materials, methods, even

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the subtle changes in the environment (e.g. temperature, surrounding ion composition and protein). At present, the corrosion processes are so complex that no study has pointed out the exact degradation mechanism in human body. The following reactions occurred is generally accepted:

$$Mg + H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow \qquad (1)$$

And it is found that magnesium and its alloys are easily oxidized to form a loose and porous magnesium oxide, which is prone to lose its protective effect on the matrix when it is in contact with the solution:

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (2)$$

Considering that the too fast degradation rate and the non-uniform degradation mainly occur at the initial stage, the interaction between MgO and the body fluid is studied to overcome these disadvantages. Since this progress is very fast and the micro degradation morphology is not easy to be observed using present macroscopic experiment, this study researches the interaction between MgO and the body fluid from microcosmic angle by a molecular dynamics simulation. What's more the body fluid is simplified as NaCl solution in consideration of that it is the main component of the blood. Further, it is vital to identify and test relevant local environment parameters which affect the adsorption behaviour significantly in a complex biological system. In this study, temperature and flow are considered, respectively.

2. Models and procedure

2.1 Models

The MD simulation model performed in this work is shown in Figure 1. In order to make the ion action more obvious, solution with relatively high concentration (4.000 mol/L) is chosen. A three-layer slab (along the z-axis) was used to represent the MgO(001) surface (McCarthy et al., 2004), whose charge density of the centre layer is analogous to those in the bulk material (Causà et al., 1986). In order to use the periodic boundary conditions, a thick enough vacuum layer is arranged on the top of the solution to interrupt the reaction between the solution and the periodic image of the metal.

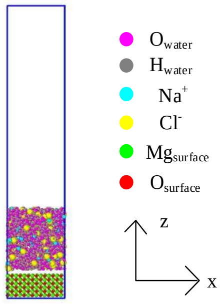


Figure 1: Model establishment and the enlarged view at the interface

The Clayff force field, developed by Cygan et al. (2004) is implemented to calculate the interaction between MgO and ions. The theory study indicates that the metal surface atoms vibrations do not have much influence on the adsorption properties of the liquid (Phan et al., 2012). Therefore, all solid atoms are frozen to improve the calculation efficiency (Chen et al., 2007). Even though the Clayff force field is derived from the SPC water model, using the SPC or the SPC/E model does not significantly affect the transferability of Clayff. In this work, SPC/E (Berendsen et al., 1987) water model is chose to simulate water. The force field parameters used in this work are summarized in Table 1. The interaction parameters between unlike atoms are determined by Berthelot-Lorentz combining rules. The cut-off distance is set to 9 Å. To compute long-range Coulombic interactions, particle mesh Ewald (PME) method is adopted.

2.2 Procedure

Molecular dynamics simulation is based on the Newton's law of motion. In this simulation, the verlet algorithm is used for the numerical integration of atomic classical equation of motion with a time step of 1 fs. Four stages are taken in performing this simulation. A Berendsen thermostat is used for 500,000 steps to make the temperature and pressure oscillation down making the system enter the steady state from the non-equilibrium state as soon as possible. Then equilibration is performed in NVT ensemble with the Nose-Hoover thermostat at target temperature and atmospheric for 500,000 steps. And then system is simulated in NVE ensemble for

1,000 time steps to analyze the stability of the system. Finally, the case is set to run in NVT ensemble for 5 ns to obtain the statistical data. When the flow is considered, a NEMD simulation is carried out.

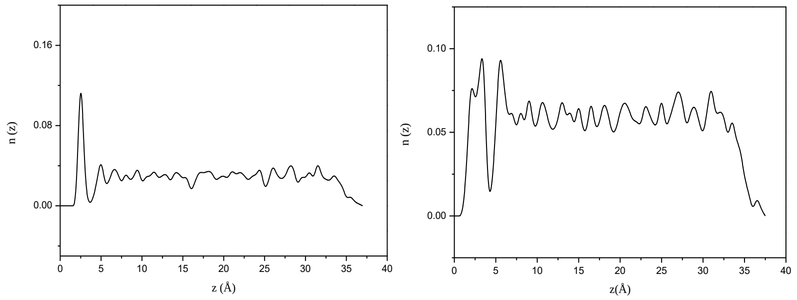
Table 1: Charge and the interaction parameter of various atoms in Clayff force field used in MD simulation

	Charge (e)	D_0 (kcal/mol)	R_0 (Å)
Mg_{surf}	1.0500	9.0298×10^{-7}	5.9090
O_{surf}	5.9090	0.1554	3.5532
Na^+	-1.0500	0.1301	2.6378
Cl^-	1.0000	0.1000	4.9388
O_{water}	-1.0000	0.1554	3.5532
H_{water}	-0.8476	0.0000	0.0000

3. Results and discussion

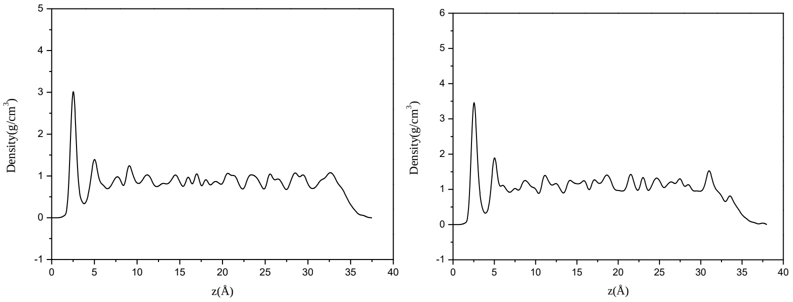
3.1 Model validation

In order to validate the present model, while the NaCl solution adsorption properties on the surface of MgO is lack, the adsorption properties of the water in the solution is first studied at 300 K. The solution is divided into several layers whose thickness is 0.5 Å perpendicular to the MgO surface. In Figure 2, atomic density profiles of oxygen atoms and hydrogen atoms of water are demonstrated as a function of the distance from the metal surface along z axis. The oxygen atomic density profile shows that there is a sharp peak at z=2.5 Å where water gathered. At the same temperature, Phan et al. (2012) found a well-defined hydration layer at z=2.55 Å whether the metal vibrated or not from the oxygen atomic density profiles. McCarthy et al. (2004) found the first hydration layer located at $z\approx2.25$ Å, using either 64 or 128 water molecules at the same temperature. There are several peaks near the metal and then the vibration weakened form a distance of 8 Å away from the substrate surface. The distribution characteristics of hydrogen support the study of Phan et al. (2012), and the multi-peaks distribution feature has also been mentioned in previous study on the interface of other solid surfaces (Zhou et al., 2018). In one word, our simulation results agree well with their results.



(a) (b)

Figure 2: Reduced number density distribution of O_{water} (a) and H_{water} (b) perpendicular to the wall direction



(a) (b)

Figure 3: The density distribution of water (a) and solution (b) perpendicular to the wall direction

Besides, from the density distribution profile (Figure 3), it can be seen that there is a solution film formed on the metal surface, due to the interaction between the solution and the metal. The solution is divided into two zones, one is adsorption zone where solution concentrated and the other is free zone where the density of the liquid in the free zone is homogeneous. The density of water and solution in the free zone is approximate to the actual liquid density (0.996 g/cm^3 for water and 1.098 g/cm^3 for solution), which shows that the free zone is not affected by the wall surface, and it also gives the fact that our calculation is close to reality.

3.2 The effect of temperature

As is well known, the body temperature is about 310 K. In fact, the temperature of each part of the body and different people will be slightly different (Sund-Levander et al., 2002). Therefore, to make the stent can be well controlled to apply to any people and any position of the body, it is important to make clear that how temperature influence the adsorption rate and adsorption capacity of body fluid at the stent surface. In this study, seven different temperatures (form 300 K to 315 K) is selected.

Figure 4a presents the variation of the number density at different temperature, and it can be seen the whole morphology is similar with above study. The position and height of the first peak at different temperature are mainly focused to study the influence of temperature on the adsorption capacity. It is found that those two parameters don't have too much difference at different temperature, the position is 0.25 nm, and the reduced height is around 0.2 Å^{-3}.

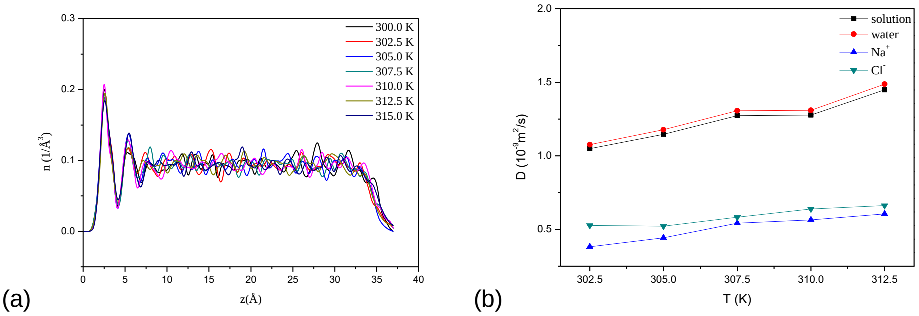


Figure 4: (a) Reduced number density distribution at different temperatures along z axis. (b) Diffusion coefficient of solution, water, Na$^+$ and Cl$^-$ at different temperatures

As for the diffusion rate, the statistics are present in Figure 4b, and we can confirm that the self-diffusion coefficient increases with increasing temperature. In the other words, the increase of temperature accelerates the adsorption kinetic energy. Furthermore, the diffusion coefficient of solution is smaller than that of water which is limited by the ions. This phenomenon indicts that water molecules are the carrier of the ions, whose properties strongly affect the transport and adsorption of ions in the solution. What's more, no matter how the temperature changes, the self-diffusion of chloride ions is larger than the sodium ions which indicates that the diffusion coefficient can be a criterion for measuring corrosiveness.

3.3 The effect of flow

Flow plays a role in mass transfer and shear stress effect which may interfere with solution adsorption at MgO surface, but it is always neglected in the immersion experiment. In this section, the influence of flow on the solution adsorption is studied.

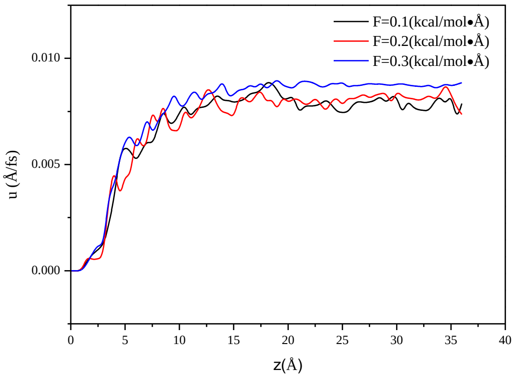


Figure 5: The distribution of x direction velocity perpendicular to the wall under different external force

The numerical simulation of pressure-driven flow of liquid NaCl solution simulation between the metal and vacuum is carried out by applying constant force (from F=0.1 kcal/(mol•Å) to F=0.3 kcal/(mol•Å)) to each atom along the x direction, after the static adsorption comes to equilibrium. A part of the work produced by an external force produces heat (Xu et al., 2004), and the other drives the flow (Duan et al., 2015). Meanwhile, the solution response to flow is analysed, including the velocity profiles, density profiles and the diffusion coefficient. Velocity profile of solution is shown in Figure 5. Distinctly, the front section of the curve is nearly in the shape of half parabola and the larger driving force leads to the curve become steeper, which is coincident with other studies about the Poisson's flow. The flat section of the curve is caused by the lack of another metal surface.

Figure 6 shows the snapshot of the case at different time. It is very obvious that the flow takes away the solution at the metal surface compared with the case without external force, making distance between the solution and the metal larger. At the same time, quantitative analysis is made. The density profiles of the solution are illustrated in Figure 7. Obviously, the position of the peak for the case of flow is lower than the still one and the peak value decreases with the increase of velocity, indicating that adsorption capacity of solution at metal wall is reduced by flow.

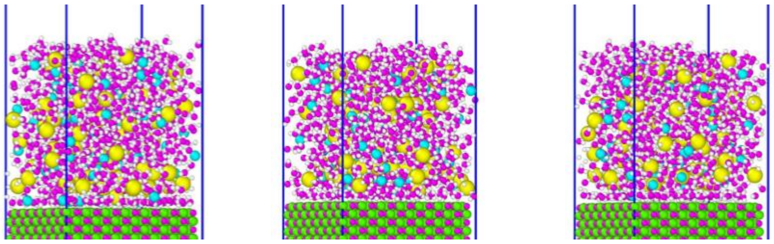

t=5.0 ns t=5.5 ns t=6.0 ns

Figure 6: The snapshots of the model at different time under external force

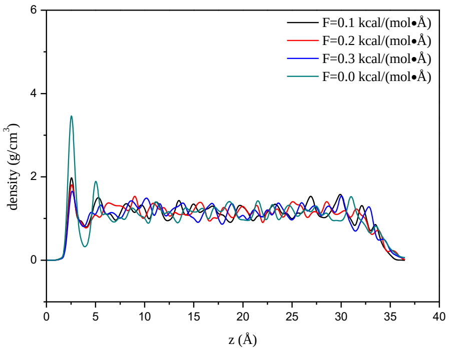


Figure 7: The density distribution of solution perpendicular to the wall under different external force

In addition, the variation of diffusion coefficient with the exertion of external force is also studied. From Table 2, it can be seen that the diffusion coefficient of solution either in the adsorption zone or the free zone increases with the increase of external force, as the liquid atoms gain an added acceleration.

Table 2: Diffusion coefficient of solution in two zones under different external force (10^{-9} m^2/s)

F (kal/(mol•Å))	0.1	0.2	0.3
Adsorption zone	2.743	2.7998	2.8168
Free zone	2.745	4.1258	5.6395

4. Conclusions

Currently the mechanism of the Magnesium alloy degradation is lack, this study could bridge a gap between laboratory results and performance in a living organism. In this study, a molecular dynamics simulation of the adsorption properties of NaCl solution on the MgO surface is conducted and the effect of temperature and flow are taken into account. The main conclusions can be drawn.

(1) There exist adsorption zones, where sharp hump forms, and free zones, where the liquid is homogeneous, in solution perpendicular to the metal surface, due to the attractive force.

(2) Temperature has little impact on the solution adsorption capacity. But, high temperature accelerates the thermal motion of the molecule.
(3) Flow can take away a part of a solution at the surface of the MgO metal, further lowers the adsorption capacity. Meanwhile, the exertion of force can accelerate the diffusion rate.

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