Molecular dynamics simulation of corrosion mitigation of iron in lead-bismuth eutectic using nitrogen as corrosion inhibitor

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Abstract. The corrosion of structural materials used in fast nuclear reactor design is a current major problem. It is due to the use of liquid metal as a coolant candidate in the heat transfer system. The liquid metal as lead-bismuth eutectic was found to make high corrosion to structural material as steel. One of the solutions of this problem is to inject some inhibitor into liquid metal. In this current work we simulate the effect of nitrogen injection as inhibitor candidate. The simulation will predict the proper concentration of injected nitrogen and also observe the microscopic structure of the material before and after injection to know the ability of nitrogen as an inhibitor. The simulation follows the molecular dynamics method and for preliminary study we use iron material rather than steel. We also use lennard-jones potential for simplification of the study. It is from our simulation we see nitrogen shows better corrosion mitigation compare with oxygen as in our previous study. The effective inhibition can be achieved by injecting at least 0.056wt.% nitrogen. This amount seems to be able to reduce the corrosion level of iron till about 99.5% for high corrosion at temperature 750 °C.

Keyword: lead-bismuth eutectic, corrosion inhibition, nitrogen, molecular dynamics

1. Introduction

Corrosion inhibitor is a substance which when added in small concentration to a corroded system will minimize or prevents that corrosion [1]. Corrosion inhibitor can be used to protect metals from corrosion attach and if we can maintain this inhibitor in an exact concentration all the time than we will be able to prevent the corrosion maximally. It is a current issue that the steels used in the fast nuclear reactor installation have been highly corroded if we use liquid lead or lead bismuth eutectic as a coolant material for heat transfer system [2]. The solution of this corrosion problem has two options: (1) finding better steel materials and/or (2) finding a corrosion inhibitor (method) to minimize and

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prevent corrosion. Especially for corrosion inhibition, there is a direction to use oxygen gas to protect a steel metal from serious corrosion attack of liquid lead or lead bismuth eutectic during high temperature interaction [2]. The degradation of steels by high corrosion effect in liquid metal is for the most part due to the dissolving of the various constituents of the steel metal by liquid metals [3]. Corrosion may be described as mainly the solution of the solid metal in the liquid metal. The control method of corrosion using oxygen is very popular in current days. Impurity such as nitrogen is another choice of inhibitor. By definition the inhibitors are substances which, when added to a chemical system in small amounts (<10 wt.%), interact with the reactants to reduce the reaction rate. Nitrogen dissolved in lead-bismuth eutectic acts as such an inhibitor through the development of a stable film reducing the dissolution rate [4].

The use of computer simulation method based on a proper material model can help us to see the possibility of elements as a promising inhibitor candidate. The molecular dynamics simulation can be used to predict the needed inhibitor concentration to prevent corrosion at maximum level. The simulation result should be able to use as a preliminary study before experiments. In our previous study we were success to show the effect of oxygen for preventing the corrosion of iron (major component of steels) in liquid lead or lead bismuth eutectic [5,6]. We show three conditions: (1) the some atoms of oxygen enter the surface of iron for possibility of protective iron-oxide layer development, (2) some oxygen atoms remain in between of iron surface and liquid metals as a barrier wall for direct interaction, and (3) some oxygen atoms experiences a precipitation in liquid metals. In this current study we want to show the possibility of nitrogen as a corrosion inhibitor in lead bismuth corrosion. We also use the classical molecular dynamics method for this study. We want to predict and compare the ability of corrosion inhibition between oxygen and nitrogen.

From experimental data the degradation of structural materials (steels) due to its direct interaction with liquid metals is very high [2,3,4]. This is not safe for application of fast nuclear reactor design and economically disadvantage. In our previous work we study the corrosion (degradation) mitigation of iron (major component of steels) by using oxygen as inhibitor agent. We also compared with experimental results [5,6]. However the simulation still shows material degradation at the surface of iron (about 30% at temperature 750 °C) [5,6]. In this current work we try to use nitrogen as inhibitor to get more improvements of corrosion mitigation. It was reported that nitrogen can also be used as an inhibitor [3,4]. However the studies of nitrogen as inhibitor of liquid metal corrosion is not much explored yet, computationally and experimentally. Many researches still focused on the oxygen as inhibitor. We hope this preliminary study can give the positive results of using nitrogen as a promising corrosion inhibitor for purpose of nuclear reactor applications.

2. Theory

In classical molecular dynamics method we solve the Newton equation of motion for specific phenomenological potential function. We solve this equation for many atoms or molecules of the material system for specific numerical integration algorithm to get the trajectories of the atoms or molecules. Based on the trajectory of all bodies and statistical mechanics then we can predict and calculate all thermodynamics properties of the system as diffusion coefficient and others. Denoting $\vec{f}_{ij}$ is the force exerted by particle *j* on particle *i* then the total force acting on particle *i* should be

$$\vec{F}_i = \sum_j \vec{f}_{ij} \tag{1}$$

When the force is conservative and for specific potential energy $u(\vec{r})$ then it follows

$$\vec{f} = -\nabla u(\vec{r}) \tag{2}$$

Then we have the total force acting on particle *i* is

$$\vec{F}_i = -\nabla \sum_j u_{ij}(\vec{r}_{ij}) \tag{3}$$

Then dynamics of Newtonian system can be described as

$$m_i\{d^2\vec{r}_i / dt^2\} = \vec{F}_i \tag{4}$$

In this equation r_i is the position of atom i, m is mass of atom i. In molecular dynamics method we solve equation (4) numerically based on specific integration algorithm that we choose. There are many algorithms we can use and one of them is the Beeman algorithm for purpose of accurate calculation. In this work we still use MOLDY molecular dynamics program for our simulation that is an open source and easy-to-use program [7].

Whereas the system of material is usually complex then we approach the interaction of all atoms of simulated material using Lennard-Jones interatomic potential for simplification of the study. In our work we simulate a metal system (iron in liquid metal with nitrogen inhibitor). There is an EAM (embedded atomic method) potential that should be better for metal simulation. However in our work we still use the classical Lennard-Jones potential as a first prediction and preliminary study. The general Lennard-Jones potential is [8]:

$$u(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] \tag{5}$$

The (12-6) LJ potential is simple physical model of interaction that approximates the interaction between a pair of neutral atoms. In this equation ε and σ are the potential parameters for pair of atom that can be determined from experimental data. The cross-interactions (ε_{AB} and σ_{AB}) for pair of different atom (A and B) can be generated by the popular Lorentz-Berthelot mixing rule [9]

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \tag{6}$$

$$\varepsilon_{AB} = \sqrt{(\varepsilon_{AA} \times \varepsilon_{BB})} \tag{7}$$

Table 1 is summary of the potential parameters that we use in our work.

Table 1. Potential parameters for Lennard-Jones Interaction.

Pair Interaction	σ (Å)	ε (eV)	References
Fe-Fe	0.400	2.319	[8]
Pb-Pb	0.191	3.189	[8]
Bi-Bi	0.059	3.050	fitting data from EAM potential [10]
N-N	0.00853	3.656	[11]
Bi-N	0.02243	3.353	equation (6 and 7)
Fe-Pb	0.2766	2.7541	equation (6 and 7)
Fe-Bi	0.15377	2.6847	equation (6 and 7)
Fe-N	0.05846	2.9877	equation (6 and 7)
Pb-Bi	0.10614	3.1194	equation (6 and 7)
Pb-N	0.04036	3.4224	equation (6 and 7)

The important physical variable that we want to calculate in this work is diffusion coefficient that can be related to corrosion rate by specific formula. The diffusion coefficient for certain temperature can be calculated from Einstein relation [12]

$$D = \lim_{t\to\infty} \frac{1}{6t} \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle = \lim_{t\to\infty} \frac{MSD}{6t} \quad (8a)$$

where

$$MSD = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle \quad (8a)$$

where t is time, T is temperature, A is activation energy for corrosion to be happen and $\mathcal{R}$ is a gas constant.

3. Simulation procedure and analysis

3.1 Details of simulations

The simulation details of our work can be described as three following steps:

(I) Model of the structure of material.
We model iron in bcc crystal structure, placed in the centre of lead-bismuth eutectic (liquid phase). Nitrogen atoms (position) placed in the liquid metal randomly. All position of atoms of material (Fe, Pb, N, Bi) should be defined as input of molecular dynamic simulation. Other inputs are: mass of atom (as in periodic table of elements), temperature (750 °C), potential parameters (σ and ε), number of integration (=160 000 step), number of atoms (Fe, Pb, N, Bi) and mesh time (0.0001 ps). The choice of this temperature is due to there are related experimental results for comparison [5,6]. The material corrosion system was composed from 10745 Fe atoms, 18309 Pb atoms and 22376 Bi atoms and for different percentage of N atoms (from total atoms of Pb, Bi and N): 0.50%, 0.75%, 1.00%, 1.50%, 2.00%, and 2.50%). The lead-bismuth eutectic is composed from 45wt% Pb and 55wt% Bi. In wt% unit then the nitrogen will be injected into lead-bismuth eutectic for different concentration: 0.037wt%, 0.056wt%, 0.074wt%, 0.111wt%, 0.150wt% and 0.187wt%.

(II) Running simulation using MOLDY.
Simulation will be done with MOLDY program. Simulation is in NPT ensemble Anderson mode, zero pressure, Nose-Hoover thermostat and in the modified Beeman integration scheme [7]. At every simulation work (same temperature, same Fe-Pb-Bi concentration and different nitrogen atom) we then will evaluate the effect of different nitrogen concentration for corrosion mitigation.

(III) Calculation of physical properties: After simulation of 160000 integration step then all needed physical properties will be calculated and determined: MSD and D(T). The simulation uses MOLDY code. For our work the diffusion coefficient and positions of atoms can be determined by using MOLDY's facilities such as MSD and Mdavpos [7].

3.2 Analysis

The purpose of physical properties calculation is to find the lowest diffusion coefficient ($D(T)$) of iron diffusion after nitrogen injection with different concentration. High diffusion of iron shows high corrosion of iron and high degradation of iron. Nitrogen is injected to reduce the diffusion of iron in liquid metal. Jmol (http://jmol.sourceforge.net) is used to view the microstructure of material before and after nitrogen injection.

4. Results and discussions

4.1 Diffusion coefficient of iron

From calculation of iron diffusion coefficient ($D(T=750°C)$) for different concentration of nitrogen (N) then we can compare our current results with our previous work [6] as shown in figure 1. In our previous work we used 44.3wt% Pb and 55.7wt% Bi whereas in our work we used 45wt% Pb and 55wt% Bi for a reason.

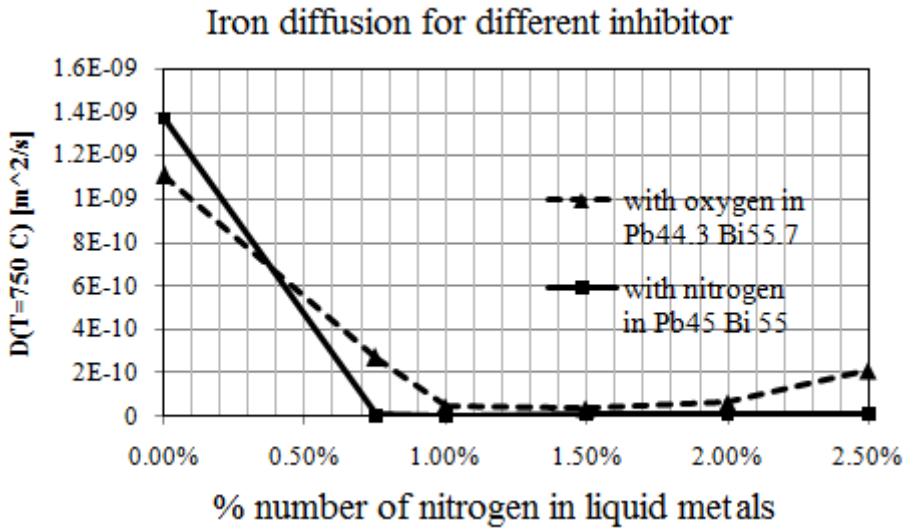

Figure 1. Iron diffusion coefficient in lead-bismuth eutectic.

From figure1 we see that using oxygen [6] and nitrogen as inhibitor then the diffusion coefficient of iron can be reduced at very low level. It means we can reduced the corrosion rate of iron till very low level. It can be seen from that figure that the use of nitrogen seems offering more stability of iron structure compare with oxygen. It seems that is easier to control nitrogen injection compare with oxygen injection because the use of oxygen seems to be controlled more carrefully at certain small concentration for narrow range (between 1.00% and 1.50%). Whereas, from the figure 1, we can see the use of nitrogen showing more flexibly of application where we can control the concentration of nitrogen in more wider ranges starting from 0.75% atoms (or 0.0562wt%) during iron-liquid metal interaction. Morover from that figure 1, we see the injection of 0.75% atoms (= 0.056wt%) of nitrogen can inhibit the corrosion about 99.51% compare without using oxygen (about 96.66%).

4.2 Structure of iron

Before simulation at temperature T = 750 °C, the iron is formed in bcc crystal structure (figure 2).

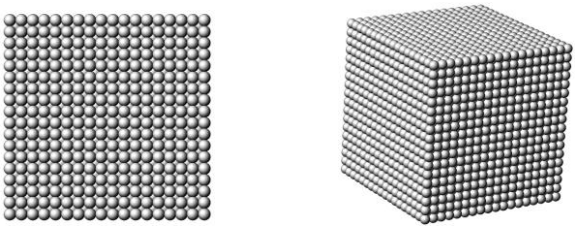

Figure 2. Structure iron before simulation (front and corner view)

After simulation T = 750 °C without nitrogen injection, the structure of iron material is as figure 3.

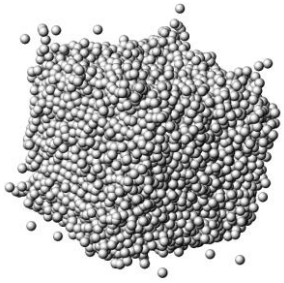

Figure 3. Iron structure without nitrogen injection

After 0.75% (= 0.056wt%) nitrogen injection into lead-bismuth eutectic then the performance of iron is as figure 4 below.

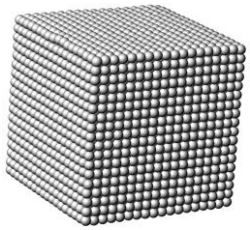

Figure 4. Iron in lead-bismuth eutectic with 0.056wt% nitrogen

Compare with 0.75% oxygen injection [6] then the structure of iron is as figure 5 below.

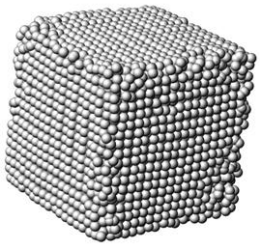

Figure 5. Structure of iron with 0.75% oxygen injection

This current work is preliminary study. The advanced research should be done to know the comprehensive understanding of corrosion mitigation using nitrogen. One of the future works is to run simulation using more accurate potential function for more accurate simulation result. However this current result is still need to be verified with experimental results. Moreover the corrosion simulation should be extended to use steels rather than iron. The application of this mitigation method (using nitrogen as corrosion inhibitor) in nuclear reactor power plant then depend on the next experimental confirmation.

5. Conclusion and remark

The corrosion mitigation using nitrogen injection seems offering more flexibility and stability to control, protect and prevent the high corrosion of iron in high temperature lead-bismuth eutectic. We

predict the use of at least 0.056wt% of nitrogen for injection it can reduce the corrosion till about 99.51%. These valuable results however need to be checked with experimental results and need to use more accurate inter-atomic potential function such as embedded atomic method potential or others.

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