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Thermodynamics and Structural Properties of Ti_3SiC_2 in Liquid Lead Coolant

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Abstract. It has been investigated by molecular dynamics method the effect of oxygen injection for Ti_3SiC_2 corrosion inhibition when this material immersed into high temperature liquid lead coolant. The diffusion coefficient of Ti_3SiC_2 was determined from mean-square-displacement simulation data. The structures of Ti_3SiC_2 during corrosion inhibition using oxygen agent were observed by Ovito vizualisation code. The simulations have been done using the Moldy molecular dynamics code. Initial material structure as input of simulation generated by Atomsk, Packmol and VESTA codes based on "file 1520829.cif" format file that taken from the crystallography open database (CoD) website. It is from our work we can show that injecting oxygen with concentration about 0.15 – 0.19 wt%, it seems can stabilize the structure of Ti_2SiC_3 maximally.

1. Introduction

For the design of LFR, it was often to use a specific metal steels as a structural material such as cladding. It is also known that many uses of steels in/under high temperature liquid lead environment showing corrosion-erosion behavior of materials [1]. These materials may often be used in liquid Lead environment at temperature about 500°C. Another material, Ti_3SiC_2, a ternary compound was known as one of the most promising candidate material for nuclear applications. This material was already

used in many industry applications however more efforts are needed to qualify its performance when compared with candidate structural stainless steel for very high temperature nuclear applications [2].

For purpose of using the Ti_3SiC_2 material in high temperature nuclear applications then many experiments have been done. Rifai and Takahashi have investigated this material to see it's corrosion behavior within high temperature molten lead-bismuth eutectic [3]. Solihin *et.al* has also investigated the titanium silicon carbide to see effect of different composition of this material [4]. What is the Titanium Silicon Carbide? Titanium Silicon Carbide (Ti_3SiC_2) is a novel structural and also functional material that is attractive due to have a high melting point, high modulus, and high-temperature oxidation resistance. These properties make it a potential material for many diverse high-temperature applications. [5].

In this work we want to study the properties of Ti_3SiC_2 material when it is immersed in the high temperature liquid lead coolant. We want to see its high corrosion behavior and how to solve this corrosion. As usually we use the molecular dynamics method to investigate this corrosion phenomena [6,7,8]. In this simulation we put the Ti_3SiC_2 material insides the liquid lead coolant at certain temperature and then see the diffusion of Ti_3SiC_2 elements. High diffusion of its elements will show high corrosion of material. To measure the level of corrosion of material we calculate the diffusion coefficient of material.

Then we do another simulation using oxygen to see the effect of oxygen to reduce the corrosion level of material. We put some different concentration of oxygen into liquid lead coolant randomly. In this primerily simulations we focus on to know: the performance of Ti_3SiC_2 material in high temperature liquid lead, the thermodynamics and structural properties and, finally the best concentration of oxygen for corrosion reduction of Ti_3SiC_2 material in liquid lead coolant.

2. Theory, Design of Material, and Method

2.1. Molecular Dynamics Simulation

2.1.1 Motion Equations of Particles

In molecular dynamics method we simulate the material under investigation for a specified period of time, an interatomic potential and a certain simulation condition (temperature, pressure, density, etc.) while creating trajectories of atoms during the simulation. Denoting f_{ij} is the force exerted by atom *j* on atom *i* then the total force acting on atom *i* of the material is

$$\vec{F}_i = \sum_j \vec{f}_{ij} \quad (1)$$

Considering the force is conservative, it is equal to the minus gradient of potential energy,

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

The equation (1) then may be written as

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

Then dynamics motion of atoms of the material system can be governed by the Newton law of motion:

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

Generally, the material system is a complex one and need to solve Eq (4) numerically. One of the popular techniques for solving the equation is the Modified Beeman algorithm. In our work we have used the MOLDY program for molecular dynamics simulation [9].

2.1.2 Interatomic Potential for Material

As a preliminary investigation of Ti_3SiC_2 we use the Lennard-Jones (LJ) potential function for simplifying the material atomics interaction as below [10]:

$$u(r) = k\varepsilon\left[(\sigma/r)^n - (\sigma/r)^m\right] \tag{5}$$

Where σ for σ_{AA} or σ_{BB} and ε for ε_{AA} or ε_{BB} are the LJ potential parameters of two similar atom. The coefficient *k* is to specify the LJ potential function,

$$k = \frac{n}{n-m}\left(\frac{n}{m}\right)^{m/(n-m)} \tag{6}$$

Taking values $n = 12$ and $m = 6$, we have the popular LJ potential,

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{7}$$

The (12-6) LJ potential is simple physical model of interaction that approximates the interaction between a pair of neutral similar atoms of material. For different type of atoms, we prepare the pair interaction using the popular Lorentz-Berthelot mixing rule:

$$\sigma_{AB} = \frac{(\sigma_{AA} + \sigma_{BB})}{2} \tag{8}$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA} \times \varepsilon_{BB}} \tag{9}$$

Table 1 shows the Lennard-Jones potential parameters using Eq.8 and Eq.9 that will be used in this work.

Table 1. List of Lennard-Jones Potential Parameters

id atom	epsilon (eV)	sigma (Å)	pair of atoms
1-1	0.0046	3.4310	# C-C
2-2	0.0102	3.4280	# O-O
3-3	0.6000	3.5000	# Pb-Pb
4-4	0.0174	3.8260	# Si-Si
5-5	0.0177	3.8000	# Ti-Ti
1-2	0.0068	3.4295	# C-O
1-3	0.0522	3.4655	# C-Pb
1-4	0.0089	3.6285	# C-Si
1-5	0.0090	3.6155	# C-Ti
2-3	0.0783	3.4640	# O-Pb
2-4	0.0133	3.6270	# O-Si
2-5	0.0134	3.6140	# O-Ti
3-4	0.1022	3.6630	# Pb-Si
3-5	0.1031	3.6500	# Pb-Ti
4-5	0.0175	3.8130	# Si-Ti

2.2 Thermodynamics and Structural Properties

To study the thermodynamic property, we can calculate the diffusion coefficient of Ti, Si and C. The corrosion of material may be defined as a structural degradation into its constituent atoms. The solubility of components Ti, C and Si may play an important role in Ti-Si-C corrosion phenomena when using heavy liquid metals as the lead [1]. To calculate the diffusion coefficient $D(T)$ we need to compute the mean square displacement below:

$$MSD = \left\langle \left| \vec{R}(t) - \vec{R}(0) \right|^2 \right\rangle \quad (10)$$

$$D(T) = \lim_{t\to\infty} MSD / 6t \quad (11)$$

where t is time, T is temperature.

To study the structural property of material, we calculate the RDF radial distribution function $g(r)$, and observe the stability of structure of material by plotting the XYZ coordinates of atoms using OVITO code [11].

2.3 Design of Material

2.3.1 Material Ti_3SiC_2

To investigate the corrosion of Ti-Si-C system we design the material system as below. We prepare the Ti_3SiC_2 material as described by file 1520829.cif [12] from the **CODB** (Crystallography Open Database) [13,14,15,16]. Using the VESTA code [17], from this 1520829.cif file we can get the structural information as below:

Material/Unit Cell : Ti_3SiC_2 (Titanium Silicon Carbide)
Lattice parameters : a = 3.07378, b = 3.07378, c = 17.68030,
alpha = 90.0, betha = 90.0, gamma = 120.0,
unit-cell volume = 144.665787 $Å^3$
Structure parameters :

		x	y	z
1	Si Si1	0.00000	0.00000	0.25000
2	Ti Ti1	0.33333	0.66667	0.36540
3	Ti Ti2	0.00000	0.00000	0.00000
4	C C1	0.66667	0.33333	0.07230.

To get "representative" material for simulation we need to duplicate this unit cell for 8x12x3 multiplication in direction x,y,z respectively. To do this we use ATOMSK code that created by Hirel [18]. The command to duplicate the unit cell of Ti_3SiC_2 like the script below:

$ atomsk 1520829.xyz -duplicate 8 12 3 TiSiC-1-8x12x3.xyz (enter)

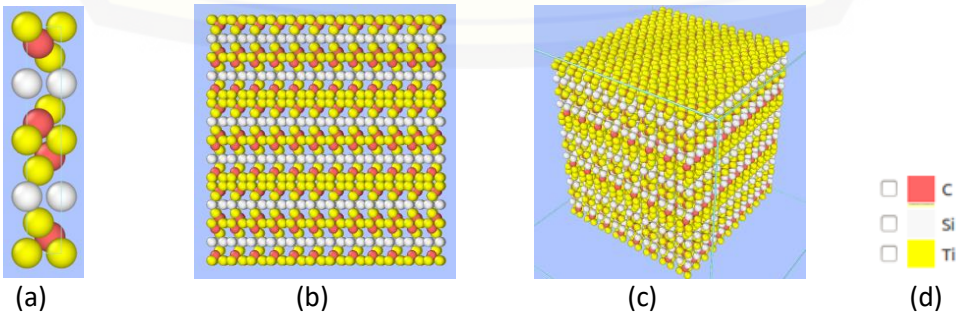


Figure 1. The Ti_3SiC_2: (a) unit cell, (b & c) Ti_3SiC_2 in 8x12x3 dimenion, (d) color code

The radial distribution function of Ti_3SiC_2 material for simulation can be seen as Fig.2 below.

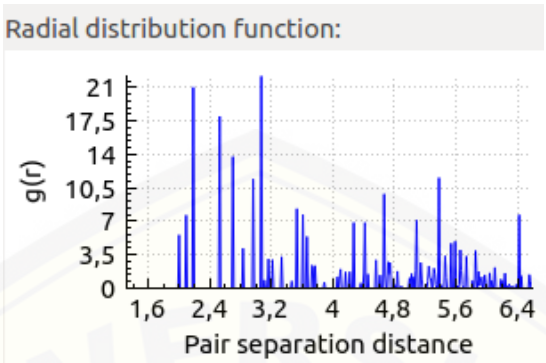
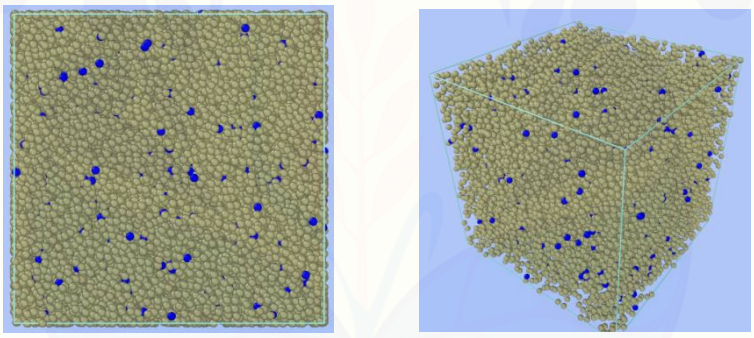


Figure 2. RDF function of Ti_3SiC_2 (by Ovito code)

2.3.2 Liquid Lead Coolant and Oxygen

To prepare the liquid lead coolant we use Packmol code [19] and its Volume Guess utility. We use distance tolerance = 2.1, atom Pb = 15093, atom O = 400 to build the Pb and Pb-O material system. The liquid lead with O (randomly) atom can be seen as in Figure 3.

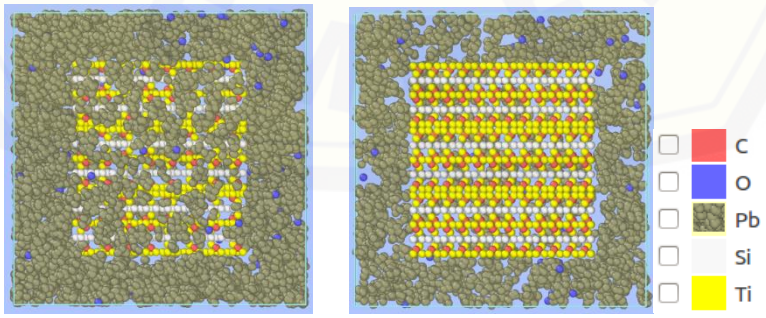


(a) (b)

Figure 3. The Pb-O material system generated by packmol

2.3.3 Ti-Si-C in Pb-O

Then we put the Ti-Si-C material in the center of PbO, using the modification utilities as supplied by ovito code.



(a) (b)

Figure 4. (a) Ti-Si-C in PbO, (b) slice picture of TiSiC-PbO

2.4 Method

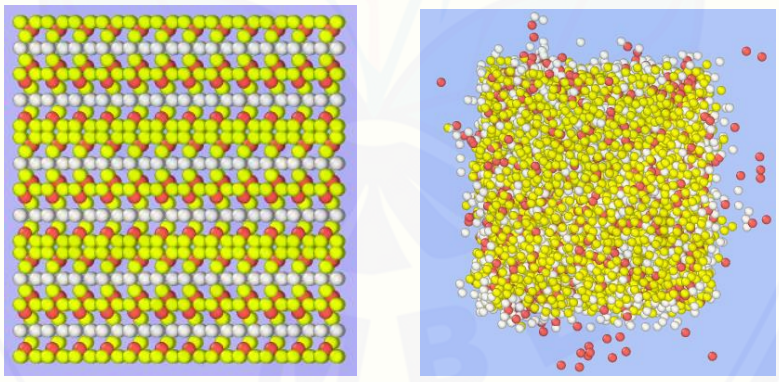
To study of corrosion and its inhibition of Ti-Si-C material system we follow this procedure:

1. Prepare two file inputs of simulation (using MOLDY code): 1. Specification file (based on Fig.4) and 2. Control file
2. Simulation of corrosion. Simulation TiSiC in liquid Pb at temperature 823 K
3. Simulation of corrosion inhibition using oxygen. TiSiC in liquid Pb with oxygen of different concentrations (wt%) at temperature 823 K
4. Using the **msd** utility of Moldy code to compute the MSD and Diffusion coefficient as described in Eq.10 and Eq.11.
5. Using the **mdavpos** utility of Moldy code to compute the final position of every atoms of material for structure calculation.
6. Using Ovito code to analyse and visualize the structure of material.

3. Results and Discussions

3.1. The Corrosion of Ti_3SiC_2

After the simulation at 823K, then the structure of Ti-S-C material shows high degradation (corrosion) as in Figure 5. Before simulation the initial structure of Ti_2SiC_3 likes Fig.5a. This structure was generated by Atomsk code with initial unit cell was taken from file 1520829.cif as described in previous. After simulation using Moldy code in NPT ensemble for temperature 823 K or 550 °C, the structure of Ti_2SiC_3 material have experienced high corrosion or degradation as Fig.5b. This should be caused by high solubility of components of Ti_2SiC_3 in liquid lead. It is popular to reduce the corrosion rate of structural material in liquid metal by injecting some inhibitor as oxygen [1]. The authors have also studied the effect oxygen for reducing the corrosion rate of iron in liquid lead [6,7,8]. Then in our work we also try to use oxygen for Ti_2SiC_3 corrosion inhibition.

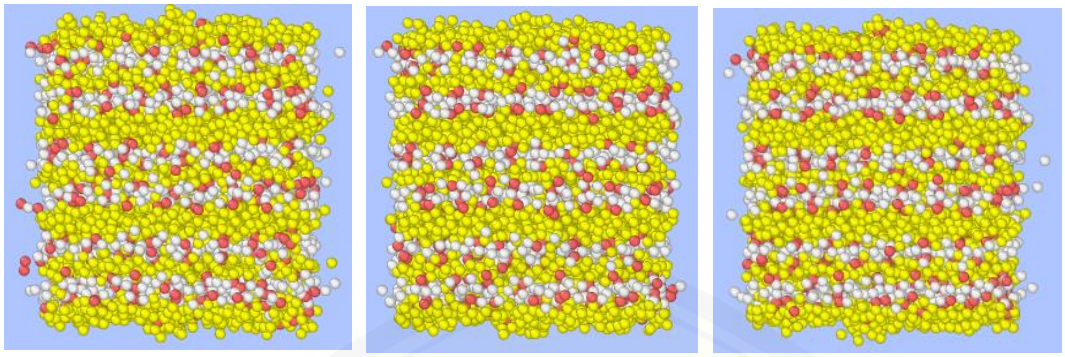


(a) (b)

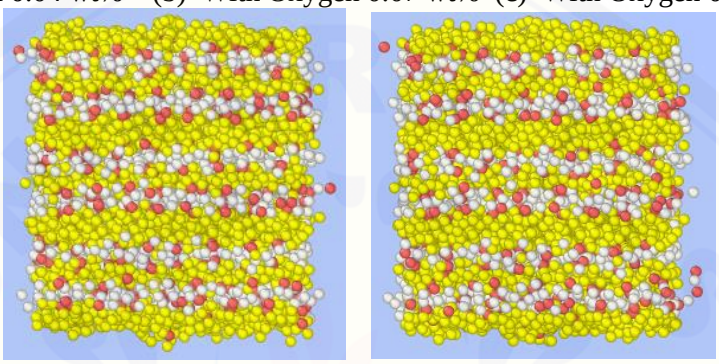
Figure 5. (a) Ti-Si-C before simulation (b) after simulation (corrosion)

3.2 Corrosion Inhibition of Ti-Si-C Using Oxygen

As effort of reducing the corrosion rate of Ti_2SiC_3 material in liquid lead then we injected the oxygen into liquid lead coolant randomly. To mixture of Pb and O atoms randomly we use packmol code. The dimension of simulation box can be predicted also by using the volume guesser utility of packmol code. We put the oxygen for several small concentrations for the purpose knowing the best proper concentration for efficient corrosion inhibition of Ti_2SiC_3. Figure 6 the pictures of effect of oxygen injection for stability of Ti_2SiC_3 structure.



(a) With Oxygen 0.04 wt% (b) With Oxygen 0.07 wt% (c) With Oxygen 0.11 wt%



(d) With Oxygen 15 wt% (e) With Oxygen 0.19 wt%.

Figure 6. Some structure of TiSiC in Liquid Lead with Oxygen

From this Fig.6 we can see that injecting even 0.04 wt% oxygen atoms have made the structure of Ti_2SiC_3 more stable compared with without oxygen injection. We can conclude which concentration of oxygen is for the best corrosion inhibition by calculating the diffusion coefficient of elements of Ti_2SiC_3.

3.3 Diffusion Coefficients

In our work we regard that the high diffusion of element then the high corrosion will appear. So, to see that there is high corrosion then we need to check if any high diffusion of element (Fe in this case). To make corrosion reduced then we need to see the diffusion of element (Fe) going to lower level after an action. In this work we put oxygen into coolant to reduce corrosion level.

The simulation of Ti-Si-C in Liquid Pb and its corrosion inhibition using oxygen injection was done with oxygen concentration 0.04 wt%, 0.07 wt%, 0.11 wt%, 0.15 wt% and 0.19 wt%. From the diffusion coefficient calculation using Eq.10 and Eq.11 then we can plot the $D(T)$ vs wt% of oxygen as Fig.8. Figure 8 is the detail of Fig.7 for oxygen concentration of 0.07wt% to 0.20 wt%.

From those pictures Fig.6,7 and 8 we can underline some important things:

1. More diffusion means more corrosion/material degradation
2. The solubility into liquid lead of Ti, Si and C shows C > Si > Ti
3. Generally, Ti, Si and C diffuse into liquid Pb
4. Injection oxygen effects to reduce the corrosion even for small quantity and there is a smallest oxygen concentration that can reduce TiSiC corrosion. This can be concluded from the diffusion coefficient of the elements as below Table 2:

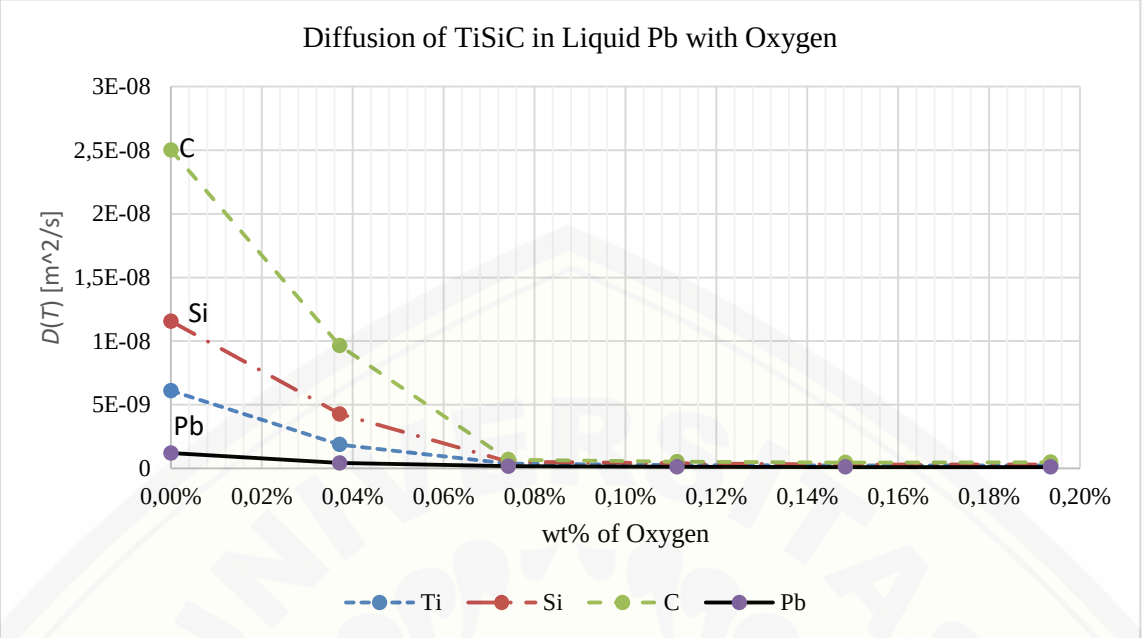


Figure 7. The graph of D(T) vs wt% of oxygen injection into liquid lead

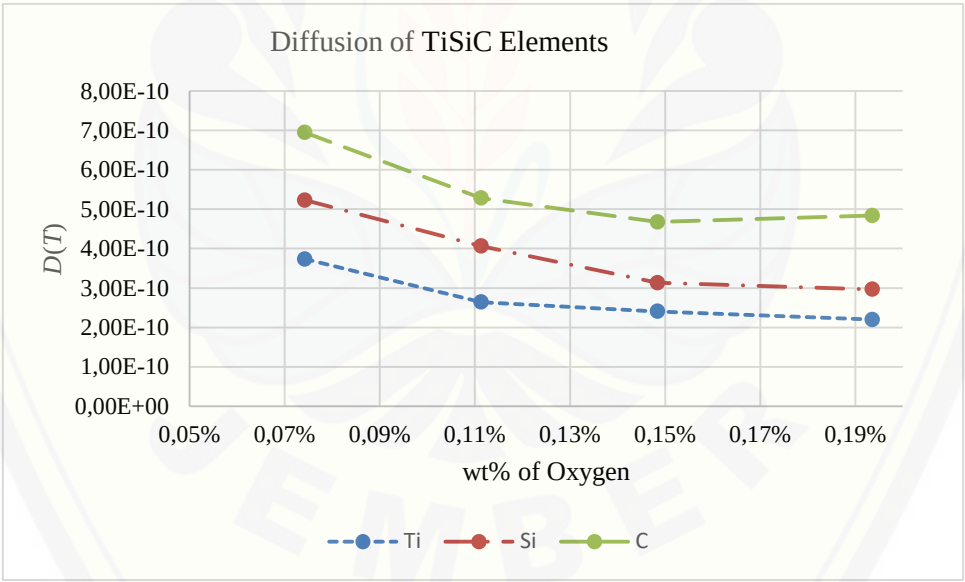


Figure 8. Diffusion of Ti,Si, C elements for wt% oxygen

Table 2. The diffusion coefficient of Ti, Si, C in Liquid Pb with oxygen

wt%	D(T) [m^2/s]			
	Ti	Si	C	Pb
0.00%	6.1098E-09	1.157E-08	2.5016E-08	1.2097E-09
0.04%	1.88E-09	4.27E-09	9.64E-09	4.22E-10
0.07%	3.73E-10	5.23E-10	6.95E-10	1.76E-10
0.11%	2.64E-10	4.06E-10	5.28E-10	1.30E-10
0.15%	2.41E-10	3.13E-10	4.67E-10	1.16E-10
0.19%	2.20E-10	2.97E-10	4.84E-10	1.11E-10

4. Conclusions

From the simulation and calculation results we can conclude several important points:

1. The Ti_2SiC_3 material has experience high corrosion in liquid lead
2. This corrosion can be inhibited by injecting oxygen atom with certain small concentration
3. Injecting oxygen with concentration about 0.15 – 0.19 wt% of total collant mass seems can stabilize the structure of Ti_2SiC_3 maximally.
4. In the liquid lead coolant, the diffusion of C > Si > Ti atom.
5. This work need more simulations to make a complete comprehensive conclusion.

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