Proceedings of International Conference on Heat Exchanger Fouling and Cleaning - 2015 (Peer-reviewed)
June 07 - 12, 2015, Enfield (Dublin), Ireland
Editors: M.R. Malayeri, H. Müller-Steinhagen and A.P. Watkinson

Published online
www.heatexchanger-fouling.com

STUDY ON PHYSICOCHEMICAL MECHANISM OF NICKEL SURFACE OXIDATION BEHAVIOR UNDER HIGH TEMPERATURE CONDITION BY USING MOLECULAR DYNAMIC METHOD

X. Lu[1], T. Ma[1], M. Zeng[1], Y. Chen[2] and Q.W. Wang[1]

[1] Xi'an Jiaotong University, Xianning West Road 28#, Xi'an, Shaanxi, 710049, P.R. China and E-mail (Corresponding author): wangqw@mail.xjtu.edu.cn
[2] University of Nevada, Las Vegas, Department of Mechanical Engineering, Las Vegas 89154-4027, United States

ABSTRACT

The surface oxidation problem of structure materials in high temperature facilities is primarily important since it is responsible for the deterioration of material properties during their service lives in engineering. This paper mainly focuses on the fundamental high temperature oxidation problem by employing reactive molecular dynamic (MD) method. The simulated oxidation reaction processes are on different nickel crystallographic orientations including Ni (001), Ni (110) and Ni (111) surfaces. The simulated exposure temperature conditions ranges from 900 K to 1500 K. Also, two different oxygen pressure conditions P_0 and $2P_0$ are calculated under 900 K and 1200 K to check the oxygen pressure effect on surface oxidation problem. All the above cases are calculated as long as 1000 ps (1 ns). The results of atomistic scale simulations reveal that higher exposure temperature and larger oxygen pressure lead to greater amount of oxide formed on nickel surfaces but the rate of increase is dependent on surface orientation. Also, atomic scale comparison between iron and nickel oxidation dynamics under 900 K shows that iron has about 6.9 times of oxide formed than nickel in the present simulated conditions.

INTRODUCTION

High temperature heat exchangers are required in many industrial systems for process reasons or aiming to attain high efficiency. Among these, the most promising fields are recuperative gas turbine and combined cycles, recuperative microturbine systems and external combustion gas turbine. The innovative solutions for high temperature heat exchanger lies on several vital aspects, including high temperature compact heat exchangers structure, thermo-fluid dynamic technology and corrosion resistance of materials. For the first two parts, thermal scientists have investigated abundantly, either from the compact innovative flow passages such as primary surface recuperator, plate-fin heat exchangers as well as printed circuit heat exchangers or to the thermo-hydraulic characteristics of supercritical CO_2 working fluids (Xu et al., 2014). However, the good corrosion/oxidation resistance and mechanical properties of structure material play a fundamental role for the facilities' safe and reliable performance under severe environments such as corrosive, high temperature, high pressure, irradiative, etc.

High temperature corrosion/oxidation of metal has long been a problem since industrial revolution emerged. Different species of metal combined with various kinds of corrosive agent make it rather complex to understand the corrosion mechanisms. For the engineering situations such as microturbine systems, gas fuels are clean working fluids without too much kinds of impurity oxidant. Hence, oxygen becomes primary attacking oxidising species during high temprature process.

In terms of the state of understanding on high temperature oxidation, a large amount of works have been implemented by experimental and theoretical methods to grasp the mechanisms of high temperature oxidation for metal. The diffusion coefficient of oxygen with metal elements such as Ni has been experimentally measured by scientists including Atkinson et al. (1986). Kinetic growth of oxidation layer has been investigated by both high temperature metal oxidation theory (Wagner, 1973) and experimental investigation. A comprehensive review on diffusion coefficient for nickel and oxygen and oxidation kinetic theories and experiment data could be found in Li (2001)'s literature. Micro-scale processes including metal ion diffusion and oxygen diffusion process as well as bond breaking/combination are of primary importance to explain physical phenomenon such as oxidation or changes in mechanical properties. But these small scale phenomenons are not easy to observe. Thanks to the raise of atomic-scale computational science, atomic-scale mechanisms of metal oxidation problem can be solved with the aid of simulation method.

Papageorgiou et. al. (2002) used the rigid iron potential model to simulate the oxygen adatom (O^{2-}) diffusion on the NiO(001) surface. Vesel et. al. (2002) presented the MD simulation results on the processes happening upon deposition of oxygen ions on the NiO(001) surface to

explain the experimental results referring to catalytic probes used in reactive plasma diagnostics. Fisher (2004) employed fixed charge MD method to simulate the reconstructed NiO surfaces using a simple two-body potential function based on the Born model of ionic solids which includes the long-range Columbic interactions and short-range terms to approximate Pauli repulsion and van der Waals attraction. However, rigid iron potential model and fixed charge model are lack of dynamic charge equilibrium calculations, which can not describe real reaction processes. Streitz et. al. (1994) developed a variable charge molecular dynamics (VCMD) model for the purpose of simulating metal-oxide system. The dynamic charge transfer between atoms where the interaction between atoms is described by the a kind of potential called Es+ which is composed of the embedded atom method (EAM) potential and an electrostatic contribution. Zhou et. al. (2001) modified and improved Streitz's model later. This VCMD model was initially used to simulate aluminum oxidation problem by Hasnaoui et. al. (2005 and 2006) and Perron et. al. (2010). Later, Garruchet et. al. (2010) investigated the initial stage of nickel oxidation by using VCMD method. Since iron has much more complex oxidate structure regimes including FeO, Fe_2O_3 and Fe_3O_4, iron oxidation reaction is harder to simulate. Soontrapa et. al. (2011) developed a set of new potential parameters for Fe_3O_4-Pb system and the results showed that the VCMD method can be used to estimate the iron oxidation problem. But, as is known to all, the oxidation reaction process involves bond breaking and combination between oxygen anions and metal cations and the models mentioned above is not able to take the bond issues into consideration. The first principle calculation and quantum chemical MD simulaiton are good ways. Das et. al. (2008) implemented the quantum chemical MD simulation to study the oxidation of bare Fe(111) and Fe-Cr(111) surfaces with strain in high temperature water. Nam et. al. (2013) determined the diffusion coefficient of oxygen in nickel and energy of the system by density functional theory. Fang et. al. (2014) predicted the oxygen diffusivities in fcc (face-centered cubic) Nickel with first-principles calculations. Recently, the reactive force filed (ReaxFF) molecular dynamics has been developed by van Duin et al. (2001) to take both charge transfer and bond breaking and combination into consideration. Also, the method can be used to simulate larger system than the quantum chemical molecular dynamics with lower computation consumption. The reactive potential parameters of iron, hydrogen and oxygen were developed by Aryanpour et. al. (2010). Pan et. al. (2011) simulated chemical reactions of iron oxidation in a damp atmospheric condition. Assowe et. al. (2012) employing the reactive force field molecular dynamic simulation to calculate the corrosion processes occurring in aqueous solutions of nickel substrate. Vasenkov et. al. (2012) investigated the Mo-based alloys under high pressure and high temperature conditions with the reactive molecular dynamics.

The present work focuses on the high temperature physicochemical mechanism of metal surface oxidation kinetics with the aid of ReaxFF model. As has been investigated (Aquaro D., 2007) that high temperature heat transfer systems have in common high materials performance requirements, typical alloy for temperature within 650 ℃ is iron-based 347 SS and when temperature inceases to higher than 700 ℃, nickel-based alloys such as Alloy 625 are important material candidates with cost effective improvement relative to 347 steel. So this work focuses nickel oxidation mechanisms and comparison between nickel and iron oxidation kinetics are compared in the last part of dicussion in this paper.

Computational method

The atomic-scale oxidation model is established, and solved with the open-source LAMMPS code (Sandia Corporation, 2003). The classical molecular dynamics with reactive force field (ReaxFF) methodology is employed to keep track of the atomic trajectory. The chemical reactions between metal ions and oxygen elements are involved within the whole oxidation system. Employed parameters in this study are from the work of Zou et al. (2015) for Ni-O potential and Aryanpour et. al. (2010) for Fe-O potential.

In a ReaxFF system, the overall energy system contains a series of energy contributions (EC), which are determined by quantum mechanics calculations. In Eq.(1), the bond energy E_{bond} describes the chemical energy between a pair of bonded atoms. Valence angle energy E_{val} accounts for the EC from valence angle; torsion rotation energy E_{tors} ensures proper dependence of the energy on torsion angle when bond order approaching trivial or bond order greater than one; van der Waals energy E_{vdW} accounts for the van der Waals interactions; and Coulomb interactions energy $E_{Coulomb}$ between all atom pairs adjusts for orbital overlap between atoms at close distances.

$$E_{total} = E_{bond} + E_{over} + E_{under} + E_{lp} + E_{val} + E_{tors} + E_{vdW} + E_{Coul} \quad (1)$$

The approach to handle charge transfer between oxygen anions and metal cations in metal–oxide simulations is to make a model of variable charge in terms of distances between atoms. The second order polynomials of temporal charges are assumed and the corresponding electrostatic energy is minimized. ReaxFF method implements many-body interactions among particles to determine molecular states, such as association or dissociation between atoms. The ReaxFF model distinguishes between σ bonds, π bonds, and ππ bonds. A bond-order (BO) between particles i and j is determined as:

$$BO'_{ij} = BO^{\sigma}_{ij} + BO^{\pi}_{ij} + BO^{\pi\pi}_{ij} = \exp\left(p_{bo1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{p_{bo2}}\right) + \exp\left(p_{bo3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{p_{bo4}}\right) + \exp\left(p_{bo5}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{bo6}}\right) \quad (2)$$

r_{ij} is the interatomic distance between particle i and j. p_{bos} (s=1,2,3,…) describe the bond order and r_0 are is the bond radius parameters for the contributions from s, p, and

double-p bonding. The bond orders are updated in each molecular calculation step. Detailed equations on how to calculate energy contributions including E_{bond}, E_{val}, E_{tors}, E_{vdW} and E_{Coul} can be found in code Manual provide by both LAMMPS (http://lammps.sandia.gov) and ReaxFF homepage(http://www.engr.psu.edu/adri/ReaxffManual.aspx).

In order to investigate the oxidation kinetics of metal surfaces, we have configured a controlled oxide growth system, which has proven to be effective for metal oxidation problems. The thickness of the metal substrate is L_z Å. Two vacuum layers are introduced on top and bottom of the metal substrate to avoid the effect of neighboring periodic image along the nonperiodic direction, just as Hasnaoui et. al (2006) did. The top and bottom vacuum space has a distance of 0.75 L_z.

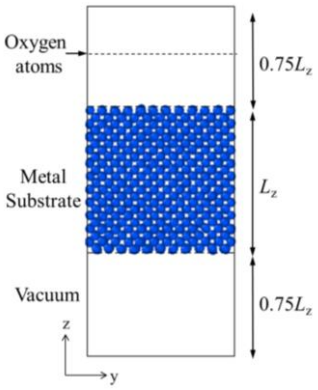


Fig. 1 Unit-cell configuration in reactive MD simulations

Periodic boundary conditions are employed in xy plane to realize infinitely repeated substrate while the fixed boundary condition is supplied in z direction. The cut-off radius, r_c, of ReaxFF potential is 10 Å. So the established vacuum zone is much larger than this to take the oxide layer growth during kinetics process and is large enough to simulate a vacuum-exposed surface.

The initially configured metal substrates are subjected to an equilibration process at the required temperature (900 K-1500 K) for 10 ps under microcanonical (NVE) ensemble and by Berendsen thermostat. After relaxation process, the oxygen atoms insertions into the simulation box are implemented when previous inserted oxygen atoms are consumed by metal atoms. The initial position of the newly inserted oxygen atoms is at an z-distance of $1.5r_c$ from the surface of metal, with randomly selected x- and y- positions. Their initial velocities are scaled from the ambient temperature along the negative z-direction as Jeon et.al. (2013) did. The time step in both equilibration process and the oxidation kinetic process is selected as 1 fs. The oxidation simulations are all as long as 1000 ps (1 ns). The present research takes the oxidation rates and corresponding oxide structure under different temperature and surface orientation into account.

RESULTS AND DISCUSSION

In the present work, cases with different crystal orientation under various temperatures have been simulated by MD method. As is summarized in Table 1.

Table 1. MD simulating cases in this work

Orientation \ Temperature	900 K	1200 K	1500 K
Ni(001)	√	√	√
Ni(110)	√	√	√
Ni(111)	√	√	√

Different crystal orientations taken into consideration in this work are shown in Fig. 2, which corresponds to three different crystal face Ni(001), Ni(110) and Ni(111).

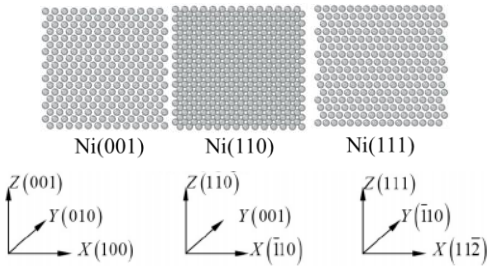
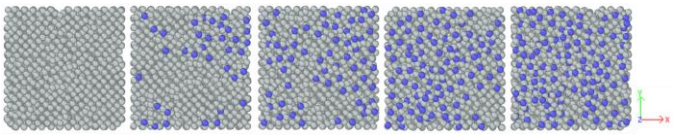


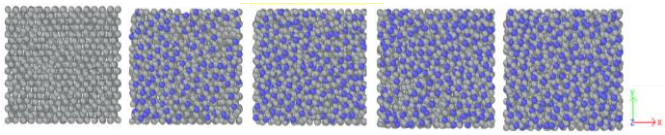
Fig. 2 Top view of crystal orientation face for Ni(001), Ni(110) and Ni(111)

The Ni(001) surface orientation metal substrate consisted of 3042 atoms, with the initial substrate with vacuum space configuration of 32.357×32.357×79.92 Å^3. The Ni(110) surface orientation metal substrate consisted of 3276 atoms, with the initial substrate with vacuum space configuration of 32.84×31.68×80.113 Å^3. The Ni(111) surface orientation metal substrate consisted of 3584 atoms, with the initial substrate with vacuum space configuration of 34.489×34.846×80.484 Å^3. The lattice constant of fcc Ni is Lα=3.52 Å.

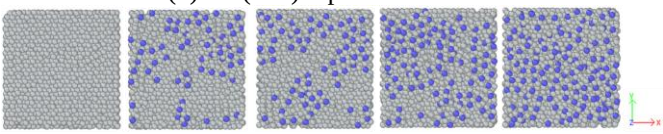
Oxidation reaction of nickel and oxygen. Take the case with 1500 K temperature as example, the atomic-scale oxidation evolutions are shown in Fig. 3. From 0 ps to 1000 ps, the oxygen atoms are absorbed to the top surface of the metal slab. It could be observed that the oxygen are preferentially react with Ni atoms whose neighbors are not oxidized, resulting that the top metal surfaces are uniformly filled with the reactant of oxygen and form an oxidation layer. Also, the oxidation process is related to the crystal orientation, where the Ni(110) surface orientation is oxidized by oxygen severer qualitatively.



(a) Ni(001) top surface view



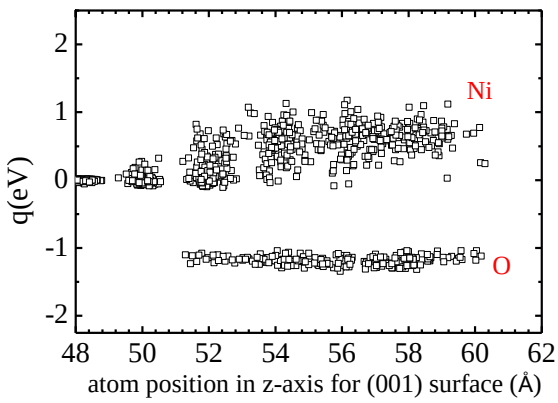
(b) Ni(110) top surface view



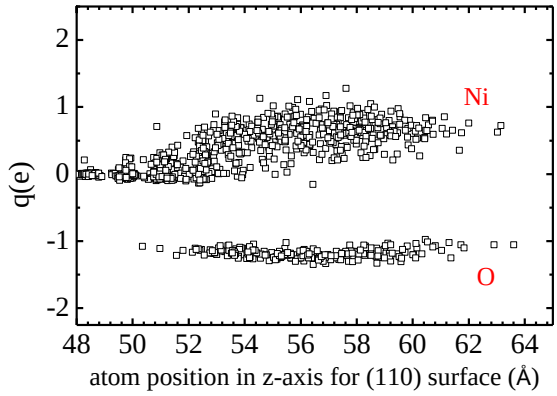
(c) Ni(111) top surface view

Fig. 3 Top view of the Ni(001), Ni(110) and Ni(111) oxide surface at 0 ps, 300 ps, 500 ps, 800 ps and 1000 ps (from left to right), T=1500 K during oxidation reaction processes

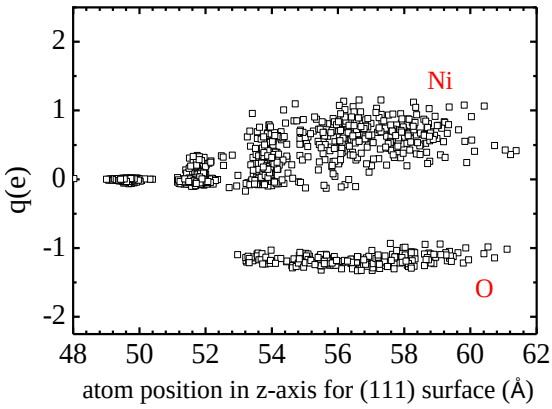
After 1000 ps oxidation process, the oxides by nickel and oxygen reaction are formed. The charge distribution of nickel and oxygen along z direction are shown in Fig. 4. From this figure, the charge carried by system atoms and the penetration depth of oxygen can be observed. The Ni cations and O anions are charged within ± 2.0e (where $e=1.6\times10^{-19}$) by charge equilibrium method. Furthermore, as has been stated in the *Computational method* part, the oxygen atoms is introduced into the simulation box at the $1.5r_c$ position when previous inserted oxygen atoms are consumed by metal atoms. The charge carried by the newly inserted oxygen atoms are zero initially. Then, since the mutual forces among nickel and oxygen atoms in the system can be calculated by ReaxFF potential functions and the corresponding charges carried by each atom can be estimated by charge equilium calculation, the newly oxygen atoms with initial charge of zero will absobed onto the nickel surface. When the oxygen is reacted, the charges of the oxygen atoms are updated as a negative value according to charge equilibrium calculation. So from Fig. 4, the positions of oxygen atoms that carry negative charges along z direction reflect the penetration depth of oxygen anions. Thus the height of oxygen film thickness could be determined. For Ni(001), the height of z direction from 51.2 Å to 61.2 Å is occupied by Ni-O oxidate; for Ni(110), the z direction position from 50.2 Å to 63.8 Å is the oxidation products; for Ni(111), the substrate from 53 Å to 60.8 Å is oxidized. The approximate oxidation thicknesses for Ni(001), Ni(110) and Ni(111) are 10 Å, 13.6 Å and 7.8 Å, respectively. Hence, the Ni(110) reaction rate is relatively high within 1000 ps at 1500 K.



(a) Ni(001) oxidation product charge distribution



(b) Ni(110) oxidation product charge distribution



(c) Ni(111) oxidation product charge distribution

Fig. 4 Charge distribution of the atom positions in z direction at 1 ns oxidation under 1500 K

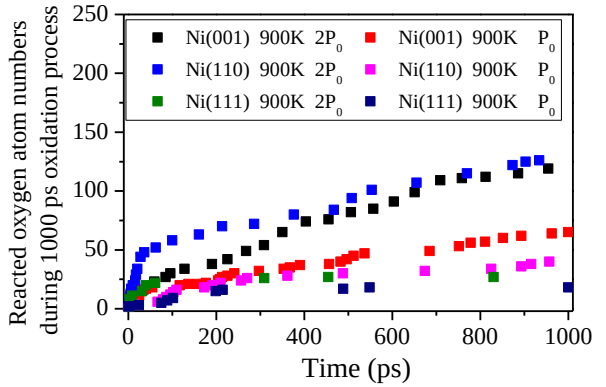
Oxidation kinetics analysis. Fig. 5 depicts the oxidation kinetics for Ni(001), Ni(110), Ni(111) under 900 K, 1200 K and 1500 K during 1000 ps. For same crystalline orientation of metal surfaces and oxidation pressure, the influence of exposure temperature on the oxidation rate is significant and higher temeperature makes the metal easier to be attacked by oxygen atoms. For Ni(001), 1.6 times of the oxygen anions are consumed at 1200 K than 900 K, while that 3.1 times oxide are formed at 1500 K than 900 K. For Ni(110), 2.3 times of the oxygen anions are consumed at 1200 K than 900 K; 4.9 times of oxygen anions are consumed at 1500 K than 900 K. For Ni(111), 1.4 times of the oxygen anions are consumed at 1200 K than 900 K; 6.9 times of oxygen anions are consumed at 1500 K than 900 K.

Furthermore, the number of attacking oxygen atoms is related to the oxidation pressure. The relationship between pressure, P, and the number of oxygen atoms, n, could be estimated by

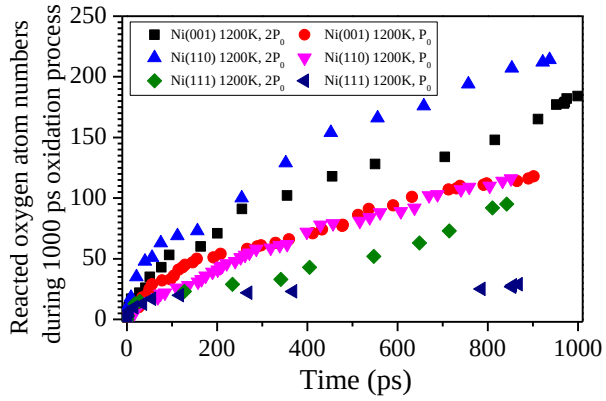
$$P=nk_BT/V \quad (3)$$

This work simulated the oxidation conditions under $P=P_0$ (9.8×10^5), and $P=2P_0$ under the temperature conditions of 900 K and 1200 K. It can be found that higher pressure (more oxygen atom attack) leads to greater amount of oxide formed on nickel surfaces. At 900 K, Ni(001) consumes 1.83 times of oxygen anions at $2P_0$ than P_0; Ni(110) consumes 2.5 times of the oxygen anions at $2P_0$ than P_0;

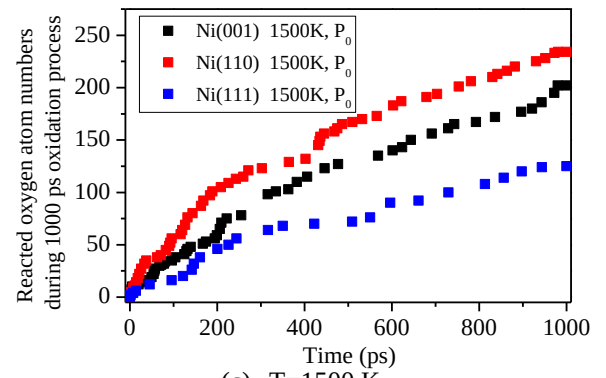
Ni(111) consumes 1.5 times of oxygen at $2P_0$ than P_0. At 1200 K, Ni(001) consumes 1.7 times of the oxygen anions at $2P_0$ than P_0; Ni(110) consumes 2 times of the oxygen anions at $2P_0$ than P_0; Ni(111) consumes 3 times of the oxygen anions at $2P_0$ than P_0. Hence, higher exposure temperature and larger oxygen pressure lead to greater amount of oxide formed on nickel surfaces but the rate of increase is dependent on surface orientation. The oxidation rate for Ni(110), T=900 K, $P=P_0$ is similar to Ni(111), T=900 K, $P=2P_0$ and for Ni(111), T=1200 K, $P=2P_0$ is lower than Ni(001) and Ni(110), T=1200 K, $P=P_0$.



(a) T=900 K



(b) T=1200 K



(c) T=1500 K

Fig. 5 Oxidation kinetic analysis with various exposure temperature and oxidation reaction pressure

Comparison between Fe and Ni oxidation. Typically, iron-based alloys can satisfy the demand for operation temperature within 650 ℃ (Aquaro D., 2007). For higher temeprature conditions above 700 ℃, higher material performance requirements are demanded. Typical alloys are 347 SS (68.7% Fe, 11.2% Ni etc.) and alloy 625 (3.2% Fe, 61.2% Ni etc.). It can be seen that with the increase of temperature, iron-based alloy can be replaced by nicel-based alloy to sustain severer temperature condition.

In this section, the microscale mechanism on how the iron and nickel perform with the attack of oxygen is discussed. The Ni(001) an Fe(001) surfaces under 900 K temperature is simulated to make comparison, as is shown in Fig. 6. The analyzes of the pair distribution function of the iron oxide at 900 K shows that the Fe-O peak at 1.65 Å. Jeon et. al (2013) have calculated the reference structure of wustite FeO, magnetite Fe_3O_4 and hematite α-Fe_2O_3, each of which has the dominant peak of 1.65 Å, 2.0 Å and 1.7 Å respectively. According to Jeon's result, the iron oxide product reveals a Fe-O peak at 1.65 Å, which is wustite FeO structure. That is because that the Fe oxidation commonly experience three stages: the first one the the thin FeO film formed and then with the iron ion in outer surface getting less, the Fe_3O_4 would form. Finally, the Fe_2O_3 film would grow on the outermost layer. For the present simulation, time scale has not sustained long enough to observe the Fe_3O_4 and Fe_2O_3 layer.

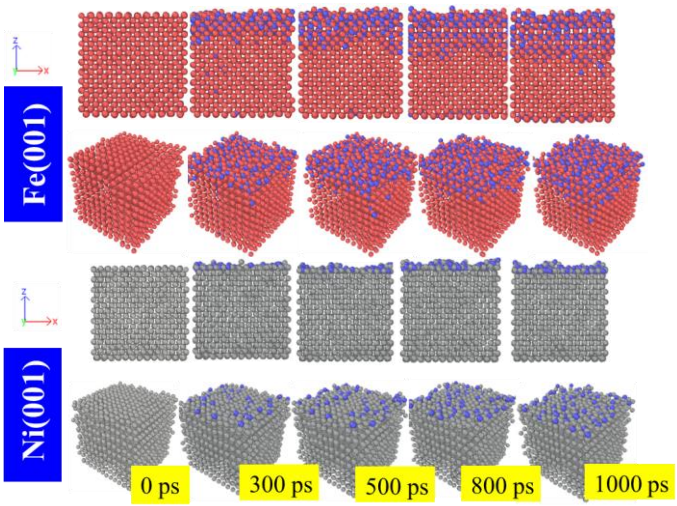


Fig. 6 Time evolution for Fe(001) and Ni(001) oxidation, T=900 K, $P=P_0$

Figure 7 shows the charge distribution of Fe(001) and Ni(001) surface under 900 K after 1000 ps oxidation reaction. It can be estimated that the oxygen penetration thickness for Fe is around 30 Å and around 3.62 Å for Ni.

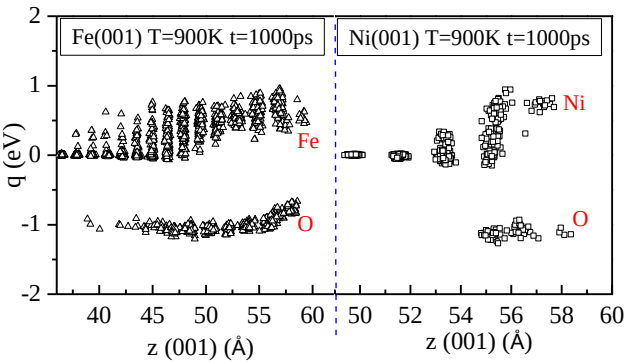


Fig. 7 Charge distribution for Fe(001) and Ni(001) surface

The total reacted oxygen atom number at 1 ns oxidation is 450 for Fe substrate and 65 for Ni substrate at the exposure temperature of 900 K, as is shown in Fig. 8. The microscopic simulation results show clearly that Fe is a more readily oxidizable substance than Ni. For this reason, although nickel-based alloys need greater initial cost than iron-based alloys, they are demanded for material property requirements because severe high temeprature oxidation problem causes bad mechanical performances of structural materials.

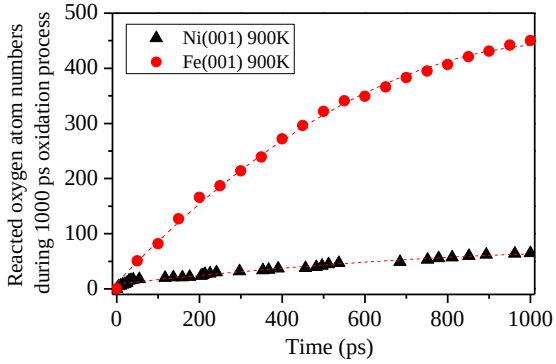


Fig. 8 Oxidation kinetic analysis for Fe(001) and Ni(001) surface, T=900 K

CONCLUSIONS AND FUTURE WORK

In this study, atomic scale physicochemical mechanisms of metal surface oxidation behavior under high temperature condition are conducted by employing the reactive molecular dynamics methodology. In this stage of investigation, it is found that the oxygen atoms are preferentially react with metal atoms whose neighbors are not oxidized, forming an uniform oxidation layer. Higher exposure temperature and larger oxygen pressure lead to greater amount of oxide formed on nickel surfaces but the rate of increase is dependent on surface orientation. For the investigated cases, nickel shows a very much better oxidation resistance than iron under high temperature.

In addition to oxidation kinetics simulations in the present work, more simulations under various temeprature conditions will be implemented to investigate the detailed quantitative informations of reaction mechanisms during the high temeprature oxidation process in the future.

.

ACKNOWLEDGEMENT

This work is supported by the Natural Science Foundation of China for International Cooperation and Exchange (No. 51120165002).

NOMENCLATURE & ABBREVIATION

BO	bond order
E_{bond}	bond energy, eV
E_{val}	Valence angle energy, eV
E_{tors}	torsion rotation energy, eV
E_{vdW}	van der Waals energy, eV
$E_{Coulomb}$	Coulomb interactions energy, eV
E_{over}	over-coordination penalty energy,eV
E_{under}	under-coordination penalty energy,eV
E_{lp}	lone-pairs energy, eV
fcc	face-centered cubic
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
Lz	length along z direction, Å
Lα	lattice constant, Å
NVE	microcanonical ensemble
p_{bos}	bond order
P	oxidation pressure, Pa
q	charge of the atoms, eV
r	interatomic distance between particle, Å
r_c	cut-off radius, Å
T	oxidation temeprature, K
x,y,z	axis directions, Å
Θ	valence angle, °
ω	torsion angle, °

Subscript

i	particle i
j	particle j
σ	the σ bonds of atom pairs
π	the π bonds of atom pairs
ππ	the ππ bonds of atom pairs

REFERENCES

Aquaro D., Pieve M., 2007, High temperature heat exchangers for power plants: Performance of advanced metallic recuperators, *Appl. Ther. Eng.* Vol. 27, pp: 389–400.

Aryanpour, M., van Duin, A. C. T., and Kubicki, J. D., 2010, Development of a ReaxFF force field for iron-oxyhydroxide systems. *J. Phys. Chem. A*, Vol. 114, pp. 6298–6307.

Assowe, O., Politano, O., Vignal, V., Arnoux, P., Diawara, B., Verners, O., and van Duin, A.C.T., 2012, Reactive molecular dynamics of the initial oxidation stages of Ni(111) in pure water: effect of an applied electric filed, *J. Phys. Chem. A*, Vol. 116, pp. 11796-11805.

Atkinson A, 1986, Oxidation of metals and associated mass transport, *The Metallurgical Society. Inc*, pp. 29-30.

Das, N. K., Ken Suzuki, K., Takeda, Y., Ogawa, K., and Shoji, T., 2008, Quantum chemical molecular dynamics study of stress corrosion cracking behavior for fcc Fe and Fe–Cr surfaces. *Corros. Sci.*, Vol.50, pp. 1701–1706.

Fang, H. Z., Shang, S. L., Wang, Y., Liu, Z. K., Alfonso, D., Alman, D. E., Shin, Y. K., Zou, C. Y., van Duin, A. C. T., Lei, Y. K., and Wang, G. F., 2014, First-principles studies on vacancy-modified interstitial diffusion mechanism of oxygen in nickel, associated with large-scale atomic simulation techniques. *J. Appl. Phys.*, Vol.115, pp. 1-8.

Fisher, C. A. J., 2004, Molecular dynamics simulations of reconstructed NiO surfaces, *Scripta Mater.*, Vol. 50, pp. 1045-1049.

Garruchet, S., Politano, O., Arnoux, P., and Vignal. V., 2010, Diffusion of oxygen in nickel: A variable charge

molecular dynamics study. *Solid State Commun.*, Vol. 150, pp.439-442.

Garruchet, S., Politano, O., Arnoux, P., and Vignal, V., 2010, A variable charge molecular dynamics study of the initial stage of nickel oxidation. *Appl. Surf. Sci.*, Vol. 256, pp. 5968–5972.

Hasnaoui, A., Politano, O., Salazar, J.M., Aral, G., Kalia, R. K., Nakano, A., and Vashishta, P., 2005, Molecular dynamics simulations of the nano-scale room-temperature oxidation of aluminum single crystals. *Surf. Sci.*, Vol. 579, pp. 47–57.

Hasnaoui, A., Politano, O., Salazar, J. M., and Aral. G., 2006, Nanoscale oxide growth on Al single crystals at low temperatures: Variable charge molecular dynamics simulations, *Phys. Rev. B*, Vol. 73, 1-13.

Jeon, B., Overmeere, Q.V., van Duin A. C. T., and Ramanathan S., 2013, Nanoscale oxidation and complex oxide growth on single crystal iron surfaces and external electric field effects, *Phys. Chem. Chem. Phys*., Vol. 15, pp. 1821-1830.

Li MS, 2001, High temperature oxidation and corrosion of metals, Metallurgical Industry Press, BeiJing, pp. 124-138.(in Chinese).

Nam, H. O., Soon H. I., Lee, K. H., and Kim, J. H., 2013, A first-principles study of the diffusion of atomic oxygen in nickel, *Corros. Sci.*, Vol.75, pp. 248–255.

Pan, T., and Xi, Y., 2011, Physicochemical nature of iron oxidation in a damp atmospheric condition. *Acta metal. Sin.(English letters)*, Vol. 24, pp. 415-422.

Papageorgiou, D. G., Karakasidis, T., and Evangelakis, G.A., 2002, Oxygen adatom diffusion on the NiO(001) surface by molecular dynamics simulation, *Physica B*, Vol. 318, pp. 211-216.

Perron, A., Garruchet, S., Politano, O., Aral, G., and Vignal, V., 2010, Oxidation of nanocrystalline aluminum by variable charge molecular dynamics. *J. Phys. Chem. Solids*, Vol. 71, pp. 119–124.

Sandia Corporation, 2003, http://lammps.sandia.gov/.

Streitz, F. H., and Mintmire, J.W., 1994, Electrostatic potentials for metal-oxide surfaces and interfaces. *Phys. Rev. B*, Vol. 50, pp. 11996-12003.

Soontrapa, C., and Chen, Y., 2011, Molecular dynamics potentials in magnetite (Fe_3O_4) modeling. *Comp. Mater. Sci.*, Vol. 50, pp. 3271–3281.

Vasenkov, A., Newsome, D., Verners, O., Russo, M. F. Jr., Zaharieva, R., and Adri C. T. van Duin, 2012, Reactive molecular dynamics study of Mo-based alloys under high-pressure, high-temperature conditions, *J. Appl. Phys.*, Vol. 112, pp. 1-13.

Vesel, A., Vamvakopoulos, E., Mozetic, M., and Evangelakis, G. A., 2002, On the microscopic aspects of oxygen ion induced sublimation of the NiO(001) surface by molecular dynamics simulation, *Physica B*, Vol. 324, pp. 261-267.

van Duin, A.C.T., S. Dasgupta, F. Lorant and W.A. Goddard, 2001, ReaxFF: a reactive force field for hydrocarbons, J. Phys. Chem. A 105, 9396-9409.

van Duin, A.C.T., ReaxFF User Manual. http://www.engr.psu.edu/adri/ReaxffManual.aspx.

Wagner C., 1973, The formation of thin oxide films on metals. *Corros. Sci.*, Vol. 13, pp.23-52.

Xu X., Ma T., Li L., Zeng M., Chen Y., Huang Y., Wang Q., 2014, Optimization of fin arrangement and channel configuration in an airfoil fin PCHE for supercritical CO_2 cycle. *Appl. Ther. Eng.*, Vol. 70, pp. 867-875.

Zou, C., Shin, Y. K., van Duin A. C. T., Fang, H. Z., and Liu, Z. K., 2015, Molecular dynamics simulations of the vacancy effect on the nickel self-diffusion, oxygen diffusion and oxidation initiation in nickel using the ReaxFF reactive force field, *Acta Mater.*, Vol. 83, pp. 102-112.

Zhou, X. W., Wadley, H. N. G., Filhol, J. S., and Neurock, M. N., 2004, Modified charge transfer–embedded atom method potential for metal/metal oxide systems. *Phys. Rev. B*, Vol. 69, pp. 1-20.

Zhou, X. W., Wadley, H.G., Johnson, R. A., Larson, D.J., Tabat, N., Cerezo, A., Petford-long, A. K., Smith, G.D.W., Clifton, P.H., Martens, R.L., and Kelly, T.F., 2001, Atomic scale structure of sputtered metal multilayers, *Acta mater*., Vol. 49, pp. 4005-4015.