

## WATER DISSOCIATION AND ADSORPTION ON NI-CR (111) BINARY ALLOY SURFACE AT 325 °C

N. Kumar Das and Tetsuo Shoji

Fracture and Reliability Research Institute, Graduate School of Engineering  
Tohoku University, Japan

### ABSTRACT

Tight-binding quantum chemical molecular dynamics study has been considered to analyze the Ni-Cr (111) surface primary stage oxidation at pressurized water reactor (PWR) environments. The present study has identified the water molecules adsorbed on top site of the surfaces by oxygen with 2.85 Å metal-oxygen bond distance. The simulated results are in well consistent with the previous theoretical study. Chromium-oxygen preferential bonds assisted to trap oxygen atoms around chromium which initiates the early stage passivation. Applied strain and defect raised the oxygen diffusion in the surface. It seems that the employed parameters heighten water dissociation. However, small atomic hydrogen diffused faster in the lattice than oxygen and it stands ahead of oxygen. Deeply diffused hydrogen is changed into negatively charged by taking electron from metallic atoms. It introduces reaction very early stage in the surface. Consequently, metal atoms become positively charged. Thus, it can originate slight repulsion in between them and works as an oxygen carrier. Thus, the process can be able to accelerate oxidation or primary stage crack initiation in surface.

**Keywords:** Strain, Atomic Defect, Water Dissociation, Oxidation, SCC Initiation.

### 1. INTRODUCTION

Nickel base alloy are widely used as structural materials for high temperature environment, such as boundary components of light water reactors (LWR), turbine blades etc. It requires very severe in-service conditions both mechanical and oxidation resistance [1]. Environmentally assisted cracking or more generally stress corrosion cracking (SCC) of structural materials is one of the limiting factors for the safe and economic operation of plants that cause an unauthorized shutdown. Recently, SCC has been found in pressurized water reactor (PWR) components such as vessel head penetrations and bottom mounted instrument nozzles fabricated with Alloy 600 and its weld metals [2, 3]. SCC initiation involves with many variables and it is a synergistic failure that is the combined actions of materials, mechanics and environment. SCC initiation is related with the localization and acceleration of oxidation at the interfaces considering microstructure, surface condition, and local environments. The localized mass transfer at the crack tip region is necessary to consider for fundamentals of SCC. Computational chemistry is a tool that can be able to incorporate with the existing methods to investigate the mechanism from atomistic level.

It is a challenging task to simulate SCC initiation of nickel-base alloy by computational chemistry. It comprised of several elements among them nickel and chromium are the major ingredients. X-ray photoelectron

spectroscopy (XPS) study of Ni-Cr alloy demonstrated that Cr is oxidized preferentially to Cr<sub>2</sub>O<sub>3</sub> initially but that Ni in the alloy is oxidized more rapidly to NiO than Ni metal [4]. Another XPS study of Alloy 600 found the chromite-rich inner layer due to inward oxygen penetration and simultaneously with outward migration of nickel [5]. On the other hand, there are several studies have been performed of the Ni/H<sub>2</sub>O, Ni/O or O<sub>2</sub> or oxygen preadsorbed Ni/H<sub>2</sub>O by first principles, molecular dynamics and experimental methods to elucidate water dissociation and adsorption phenomena [6-11]. In one of the studies suggested that preadsorbed oxygen plays an important role in industrial reactions on transition metal catalysts. The adhesion of water to nickel surfaces is very weak. Most recently, we have successfully applied multiscale methods to examine the initial stage oxidation of Ni-Cr (111) surface with different stress intensity [12]. Stress intensity significantly increases oxygen diffusivity in the surface subsequently it can intensify crack initiation. In this paper, we adhere to a tight-binding quantum chemical molecular (QCMD) approach to the early stage oxidation of the Ni-Cr binary alloy with applied external strain and atomic defect on the surfaces. Mainly we focus on the water dissociation and diffusion process because the surface reaction dynamics has not been considered so far.

### 2. COMPUTATIONAL DETAILS

We have designed well set of parameters for analyz-

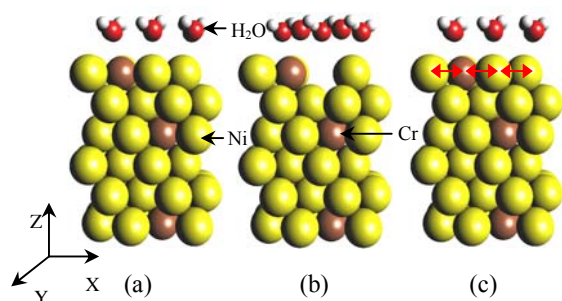


Fig 1. Slab surfaces for simulations (a) Ni-Cr (111) regular surface, (b) Ni-Cr (111) defect surface and (c) Ni-Cr (111) surface with applied strain.

-ing reaction dynamics of binary or ternary nickel base alloy or austenitic stainless steels. Diatomic calculation have been performed followed by the bulk systems by considering several parameters such as binding energy, equilibrium bond distance, cohesive energy, lattice constant and so on. The set of parameters are well consistent with the experimental and first principles calculated data, as for example, the calculated cohesive energy of nickel is 4.42 eV and the experimental value is 4.44 eV. More details about the parameterization can be seen elsewhere [13]. Tight-binding QCMD code ‘colors’ developed by Tohoku University has been employed for the water dissociation and adsorption on Ni-Cr (111) binary alloy surface at high temperature environment. This code is five thousand times faster than conventional density functional theory (DFT) and it can handle reaction dynamics of metal surfaces efficiently. Ni-Cr surface crystal structure has been created by using the software Material Studio. Figure 1 shows the slab models of Ni-Cr binary alloy. It consists of 48 atoms (42 of Ni and 6 of Cr atoms) with monolayer six water molecules embedded on the surfaces. Water molecules placed 3 Å away from the surfaces. To analyze the strain and defect dependence of the chemical reaction with water, the metal structure deformed. The uniaxial tensile strain has been applied by extending one percent of lattice constant along the x-axis of metallic surfaces as well as one atomic defect introduced on top of surface. Total 5000 number of simulation steps have been carried out where each step was 0.2 femto second (fs) with the Verlet algorithm. The advantage of this algorithm is that it requires less computer memory, because only one set of positions, forces and velocities need to be carried at any one time. The ensemble for this simulation was constant volume and constant temperature (NVT) and the temperature is controlled by using scaling the atom velocities. Temperature was considered 325 °C represents the PWR condition and atmospheric pressure was assigned.

### 3. RESULTS

DFT is the most precise tools to analyze the surface phenomena at the atomic level but it requires huge computational power and it is expensive. On the contrary, tight-binding self consistent field is another worthy method to describe the dynamical features of surfaces.

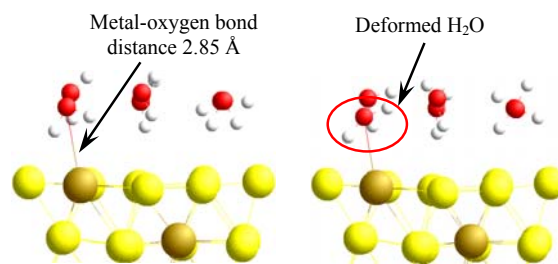


Fig 2. Birds eye view of water adsorbed surface.

### 3.1 Water Dissociation and Diffusion

Water molecules moved toward the metal surfaces with respect to time of simulation. It adsorbed on top site with the oxygen due to the most stable site. Theoretical and experimental studies have demonstrated that top site is the most stable for water absorption [13]. It stays on top site and starts deformation quickly. Figure 2 shows a close view of simulated surfaces where it is clearly observe the water adsorption and deformation on Ni-Cr surface. The thermal desorption spectroscopy study demonstrated that water molecules adsorbed molecularly on the Ni (111) surface from 165 K at low coverage to 170 K at saturation [10] and it can absorb up to 260 K when oxygen-predosed on surface. The results recommend that water molecules dissociate on the surface more than 260 K. The higher temperature initiates water dissociation quickly at the same time, metal atoms commence to dissolution from the surfaces. The bond distance in between the oxygen of adsorbed water molecule and metal atom is found 2.85 Å (see Fig. 2). A. Michaelides *et al.* have proposed that the metal-oxygen bond distance is 2.29 – 3.02 Å [14] and LEED results have demonstrated a bond distance 2.23 Å of Ni-O [15], in favor of the present calculation. H, O and OH generated from dissociation of water molecules. Hydrogen mobility is higher than other elements due to small atomic size. It can penetrate easily through interstitial sites. Several hydrogen atoms diffuse in the surface shortly and rest of them remain above the surface. It can be absorbed by the solution. Metal water interaction raises the dissociation rate of water molecules with respect to time. It is reasonable to diffuse these elements in the surfaces; subsequently surface can be modified. Figure 3 shows that oxygen concentration is significantly high around the chromium atom. It is well

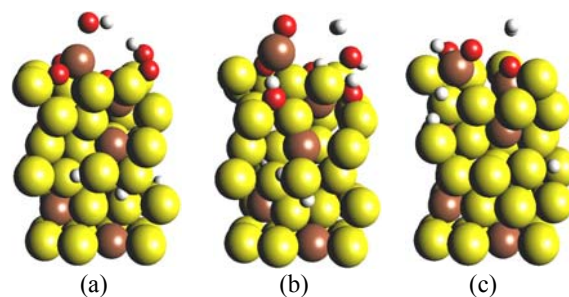


Fig 3. The calculated surface morphologies of (a) Ni-Cr regular surface, (b) Ni-Cr regular surface with applied strain and (c) Ni-Cr defect surface, after 1000 fs.

known mechanism both experimentally and theoretically that chromium forms a protective passive film by making preferential bonds with oxygen. It is difficult to quantify from the present study due to the limitation of time and length scale but qualitatively simulated results observe the initiation of passive film formation on the surface. The calculated surfaces show that the chromium moves upward to the surface because it dissolves faster than nickel atoms. Scanning electron microscopy (SEM) analysis of alloy 600 examined that chromium and iron are selectively dissolved and nickel remain at the surface of matrix [16]. The results obtained by the simulation are qualitatively well consistent with SEM study. Cr-O diatomic binding energy (4.78 eV/mole) is higher than Ni-O (3.79 eV/mole); therefore, it can assist oxygen to make preferential bond with chromium [17]. Moreover, the cohesive energy of nickel is higher than chromium that may lessen segregation of nickel atoms from the surface. Applied strain and atomic defect enhance oxygen diffusivity in the lattice along the z-axis. Figure 4 shows oxygen mean square displacement (MSD) of different surfaces. The value clearly replied that oxygen diffusivity in regular surface is lower than the other two surfaces. Thus, water dissociation on the surface is augmented by these two localized parameters. Applied strain or defects generated free more space in the lattice that helps to move metallic atoms frequently during the reaction occur. Oxygen adsorption weakens the metallic bond as a consequence metal-metal bond breakage and can easily dissolve from the surface.

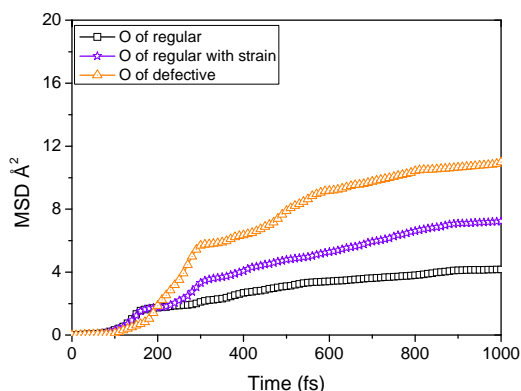


Fig 4. MSD of oxygen for different Ni-Cr surfaces.

From the fundamental aspects, essential element hydrogen is necessary to look at seriously. It diffuses faster than oxygen or any other species in addition to it can trap into interstitial sites owing to small atomic size. It has detrimental effect on materials properties such as hydrogen embrittlement, hydrogen oxidation etc. The simulated surfaces demonstrated that the dissociated hydrogen travel ahead of the oxygen or OH. These atoms can be able to lessen the strength of metallic bonds. Thus, it can empower oxygen diffusion in the metal.

### 3.2 Atomic Trajectories

Trajectory is a process to describe the dynamical features of atoms. Figure 5 shows the atomic advance-

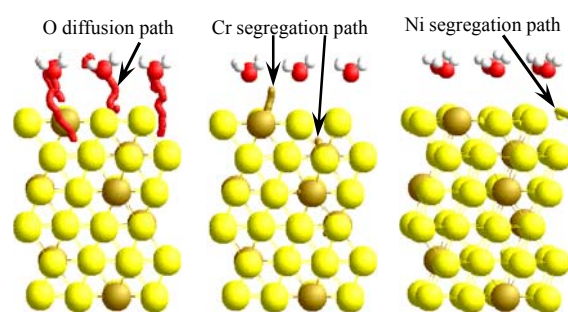


Fig 5. Simulated atomic trajectories.

ment during the simulation. Water molecules adsorb on top site but the dissociated oxygen diffuses through the hollow site. The experimental and theoretical studies examined that the hollow site is energetically most preferential for oxygen adsorption [8]. Oxygen adsorption and diffusion path in the present study are in good agreement with the previous observation. The dissociated oxygen trajectory shows that atoms remain around the chromium and the bonding decelerates further diffusion. The chromium atoms move upward from the surface whereas nickel segregation rate is very slow.

### 3.3 Mulliken Population Analysis

Atomic charge with diffusion is calculated by using Mulliken population analysis, as shown in Fig. 6. The calculated results for other surfaces become harmonious with this figure, provided that it is not necessary to show them here. At the elementary stage, chromium and hydrogen are positive in charge and oxygen atoms are negative in charge besides, nickel atoms are not designated to any remarkable charges. The atomic charge modifies with respect to time evolution. The negative oxygen atoms are strengthening value by taking electrons from metals and metal atoms are becoming positively charged. Especially, chromium atoms present noteworthy positive in charge. Figure 6 with the simulated surface of 700 fs suggests that the top three layers of metal atom content higher charges than the bottom layers. So, the top layer atoms are taking part actively in the reaction process at the beginning stage that raises electron transfer. Hydrogen atom on top of surfaces exhibits positively charged whereas the penetrated hydrogen notices negatively charged. Hydrogen negative charge in metal is interesting but not surprising and it is well consistent with our previous

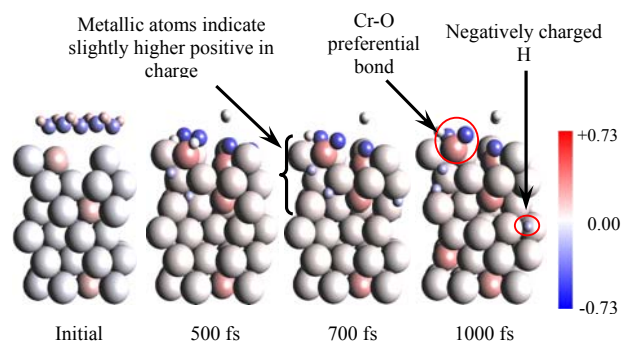


Fig 6. Atomic charge variation with time evolution.

results [18,19]. Although, the positively charged hydrogen is well known in the literature and it acts for decohesion. Hydrogen decohesion mechanism cause embrittlement. However, three highly simplified models have been proposed by Fiks in 1959 [20]. The models are: the protonic, the hydrogenic and the anionic. According to the anionic model, hydrogen receives electron from metal and change into negative in charge. Thus, the deeply diffused hydrogen interacts with metallic atom comparatively longer period of time and it takes electron from metal. The electron transfer process activates the surface chemically for further reaction. It makes easier for oxygen diffusion accordingly oxidation accelerates.

#### 4. IMPLICATIONS

The overall material degradation behavior involves many interrelated and often complex processes and reactions [21]. Fundamental aspects of the reaction mechanism comprise as follows: a) adsorption at the surface, b) diffusion or transport of reactants, c) film growth, development of voids or porosity, and d) stress produce in the scale and subsequent deformation or failure. The elucidation of cracking or material degradation requires atomistic fundamental knowledge of surfaces. The elements adsorb on the metal surface to lose metal-metal bond strength. The high metal-oxygen bond energy initiates the nucleation and new bond formation in between metal and oxygen. The process is essentially required to form protective passive film on the surface. Higher diffusivity of environmental species resulting in accelerates the surface oxidation. The protective film rupture may not necessary to crack advancement. Film degradation losing protective capability can cause a metal dissolution through the degraded film as well as film rupture [22]. Thus, the oxidation reaction, including anodic dissolution and formation of an oxide film, is a crucial process in crack initiation. The elements which can enhance oxidation and degrade the passive film stability, in the long run it is detrimental for material in the SCC standpoint

#### 5. CONCLUSIONS

The calculated results reveal that the water molecules adsorbed on top site of the surfaces by oxygen. The metal oxygen bond distance is 2.85 Å, showing good agreement with the previous theoretical study. Oxygen concentration is substantially high around the chromium. It reveals the early stage passivation initiation. We detect that the chromium dissolution rate is higher than nickel. Lower nickel segregation might help to form a nickel enrich inner oxide layer. Moreover, hydrogen atoms diffused faster in the lattice than oxygen and it stands ahead of oxygen. The applied strain and atomic defect heighten the permeation of hydrogen and oxygen atoms into lattice. Water dissociation on the surface is increased by these two localized parameters. It directly correlates with the surface oxidation. The initially penetrated hydrogen weakens the metallic bond by taking electron and the process make easier for oxygen further permeation in the surface. Negative in charge hydrogen commencing surface oxidation and consequently, it

works as an oxygen carrier. Therefore, it can accelerate oxidation and/or very beginning stage of SCC initiation.

#### 6. ACKNOWLEDGEMENTS

This work has been performed under the support of Grant-in-Aid for Scientific Research (S) 17106002, Japan Society for the Promotion of Science, and the support of the PEACE E program jointly supported EDF, EPRI, SKI, TEPCO, KEPCO, Tohoku EPCO, JAPCO, HITACHI Ltd., MHI, TOSHIBA Co., and IHI.

#### 7. REFERENCES

1. Douglas, D. L., 1995, "A Critique of Internal Oxidation in Alloys during the Post-Wagner Era", *Oxidation of Metals*, 44:81-111.
2. Scott, P. M. and Benhamou, C., 2001, "An Overview of Recent Observation and Interpretation of IGSCC in Nickel base Alloys in PWR Primary Water", *Proc.10<sup>th</sup> Int. Symp. On Environmental Degradation Materials Nuclear Power Systems – Water Reactors*, NACE, CDROM.
3. Scott, P. M. and Combrade, P., 2003, "On the Mechanism of Stress Corrosion Cracking Initiation and Growth in Alloy 600 Exposed to PWR Primary Water", *Proc.11<sup>th</sup> Int. Symp. On Environmental Degradation Materials Nuclear Power Systems – Water Reactors*, ANS, CDROM.
4. Jeng, S. P., Holloway, P. H. and Batich, C. D., 1990, "Surface Passivation of Ni/Cr Alloy at Room Temperature", *Surface Science*, 227:278-290.
5. Ziemniak, S. E. and Hanson, M., 2006, "Corrosion Behavior of NiCrFe Alloy 600 in High Temperature, Hydrogenated Water", *Corrosion Science*, 48:498-521.
6. Sebastiani, D. and Site, L. D., 2005, "Adsorption of Water Molecules on Flat and Stepped Nickel Surfaces from First Principles", *Journal of Chemical Theory and Computation*, 1:78-82.
7. Wang, G. C., Tao, S. X. and Bu, X. H., 2006, "A Systematic Theoretical Study of Water Dissociation on Clean and Oxygen-preadsorbed Transition Metals", *Journal of Catalysis*, 244:10-16.
8. Yamagishi, S., Jenkins, S. J. and King, D. A., 2003, "First Principles Studies of Chemisorbed O on Ni{111}", *Surface Science*, 543:12-18.
9. Mittendorfer, F., Eichler, A. and Hafner, J., 1999, "Molecular Precursors in the Dissociative Adsorption of O<sub>2</sub> on Ni (111)", *Surface Science*, 433-435:756-760.
10. Pache, T., Steinrück, H. -P., Huber, W. and Menzel, D., 1989, "The Adsorption of H<sub>2</sub>O on Clean and Oxygen precovered Ni(111) Studied by ARUPS and TPD", *Surface Science*, 224:195-214.
11. Netzer, F. P. and Madey, T. E., 1981, "Coadsorption-Induced Azimuthal Ordering in Molecular Adsorbate Layers: H<sub>2</sub>O and NH<sub>3</sub> on Oxygen-Precovered Ni(111)", *Physical Review Letters*, 47:928-931.
12. Das, N. K., Tirtom, I. and Shoji, T., 2009, "A Multiscale Modelling Study of Ni-Cr Crack Tip Initial Stage Oxidation at Different Stress Intensity",

- Materials Chemistry and Physics, under review.
13. Das, N. K., 2008, Fundamental Mechanistic Study of Stress Corrosion Cracking – Quantum Chemical Molecular Dynamics Approach”, Ph.D. thesis, Tohoku University, Sendai, Japan.
  14. Held, G. and Menzel, D., 1994, “The structure of the  $p(\sqrt{3} \times \sqrt{3})R30^\circ$  bilayer of  $D_2O$  on  $Ru(001)$ ”, Surface Science, 316: 92-102.
  15. Michaelides, A., Ranea, V. A., Andres, P. L. D. and King, D. A., 2003, “General model for water monomer adsorption on closed-packed transition and noble metal surfaces”, Physical Review Letters, 90:216102.
  16. Terachi, T., Totsuka, N., Yamada, T., Nakagawa, T., Deguchi, H., Horiuchi, M., and Oshitani, M., 2003, “Influence of Dissolved Hydrogen on Structure of Oxide Film on Alloy 600 Formed in Primary Water of Pressurized Water Reactors”, 40:509-516.
  17. Lide, D. R., Editor-in-Chief, 2007-2008, “CRC Hand Book of Chemistry and Physics”, 88<sup>th</sup> Edition, New York, USA.
  18. Das, N., K., 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”, Corrosion Science, 50:1701-1706.
  19. Das, N., K., Suzuki, K., Ogawa, K. and Shoji, T., 2009, “Early Stage SCC Initiation Analysis of FCC Fe-Cr-Ni Ternary Alloy at 288 °C: A Quantum Chemical Molecular Dynamics Approach”, Corrosion Science, 51: 908-913.
  20. Fiks, V. B., 1959, Soviet Physics Solid State, 14.
  21. Kofstad, P., 1988, “High Temperature Corrosion”, Elsevier, London.
  22. Takeda, Y., 2004, “Mechanistic Study of Intergranular Stress Corrosion Cracking in High Temperature Water Based on Electric Properties of Oxide Film”, PhD Thesis, Tohoku University, Sendai, Japan.

## 8. MAILING ADDRESS

Nishith Kumar Das  
 Fracture and Reliability Research Institute,  
 Graduate School of Engineering  
 Tohoku University,  
 Sendai 980-8579 Japan