Fundamental Mechanistic Study of Stress Coroosion Cracking-Quantum Chemical Molecular Dynamics Approach(-)

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論 文 内 容 要 旨

1 INTRODUCTION

Stress corrosion cracking (SCC) has been attributed to many engineering failures, some of which have resulted in loss of life and others in significant economic losses. Many experimental as well as mechanistic modeling efforts have been made to try to solve the light water reactors SCC problem but it still remains unclear [1,2]. It is difficult to explain in details such a complex problem like SCC. Recent, analytical transmission electron microscope (ATEM) study showed that the crack tip is as narrow as 1-5 nm [3]. This narrow region is believed to be the molecular domain which is very effective zone to understand the SCC mechanism. This molecular domain region is difficult to analyze by experiment to clarify this phenomena. Most of the SCC phenomena have been observed in face centered cubic (fcc) metals and alloys because of their limited slip system and so on. Many SCC has been experienced in austenitic stainless steels and Ni-base alloys in light water reactor (LWR) environments. For this reason, it is rational to consider the fcc structure for all cases even in case of iron structure calculations. This work is focused on trying to better understand the fundamental solid state oxidation mechanism of fcc Fe (111), Fe-Cr (111), and Fe-Cr-Ni (111) surfaces considering nanoscale SCC crack tip domain at high temperature and by considering oxidation phenomenon theoretically design the expected SCC resistant Ni-base alloy.

2 OPTIMIZATION OF PARAMETERS

Tight-binding method being used for the analysis of chemical reaction dynamics on the metal surface for using the slab model, with a density functional theory (DFT) method being used for understanding the adsorption mechanism of metal surface along with the screening of alloy candidates which is expected to be resistant to SCC. A suitable set of parameters is very important for the tight-binding calculation of alloys and it is the most difficult task. We have obtained diatomic properties and compared with the DFT and experimental results. By considering these parameters, bulk systems have been analyzed and compared with the available results. As for example, the calculated cohesive energy for the chromium metallic bulk system is 3.98 eV, the value shows well consistency with the experimental value 4.10 eV. On the other hand, calculated atomic oxygen mean square displacement (MSD) value 0.03 $Å^2$, is close to the value observed by XRD 0.01 $Å^2$ [4]. The set of parameters have been selected for the alloys with water interaction at BWR conditions.

3 STRESS CORROSION CRACKING STUDY OF FCC Fe, Fe-Cr, AND Fe-Cr-Ni ALLOYS

From computational chemistry point of view, the simplest and most natural model of a surface is a cluster of metal atoms. The cluster model has been used to treat the chemisorption or diffusion phenomena on transitional metal surfaces for at least last two decades. This method has been done both of *ab initio* and tight-binding self consistent field (SCF) methods. Real materials composed of several kinds of elements and systems are more complex. The logical first step in moving towards the study of more realistic materials is the study of single crystal binary or ternary models with water at high temperature conditions. Mechanical factor such as strain is necessary to consider within this kind of environment to understand reaction phenomena at the atomistic level. Hence, in the
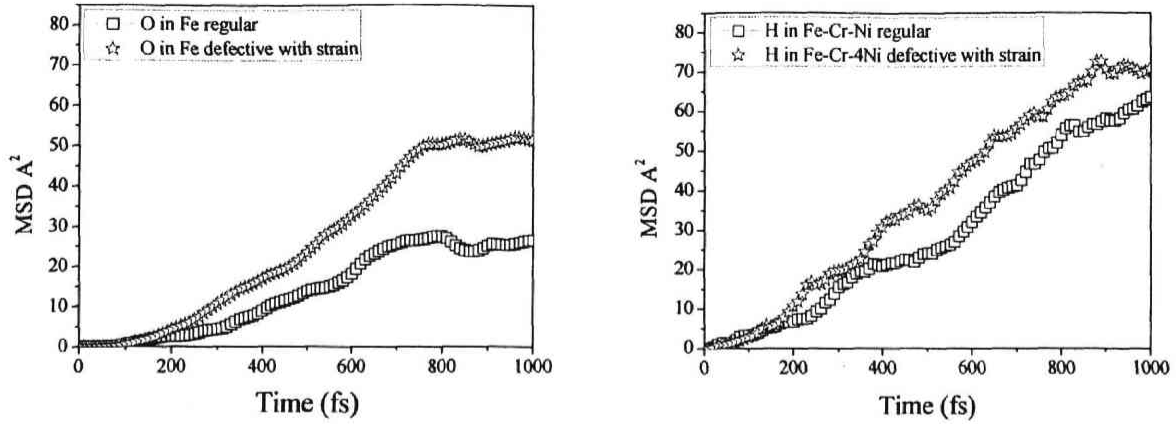
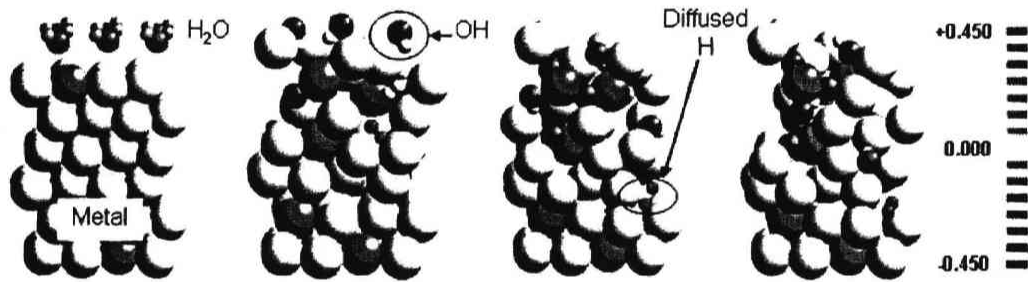Figure 1 MSD comparison of prefect matrix and defective with strain matrix.

Figure 2 Mulliken population of matrixes.

present study, quantum chemical molecular dynamics (QCMD) simulation is applied for the initial stages of the reaction process on the Fe, Fe-Cr, and Fe-Cr-Ni regular and defective matrixes with and without strain in high temperature water. The objective of this study is to investigate solid state oxidation of Fe (111), Fe-Cr (111) and Fe-Cr-Ni matrixes at high temperature environment by considering QCMD. The tight-binding calculations have been performed by using 'colors' code with slab model which is consists of 48 metallic atoms with monolayer six water molecules. At the early stage, water is decomposed and diffused into the matrixes with respect to time which indicates the surface oxidized and metal atom segregate from the surface. Fe and Cr segregated from the matrixes whereas Ni atoms slightly move upward. This phenomenon revealed the Ni enrichment at the crack tip region. Addition of Ni reduced the oxygen MSD value due to nickel oxygen strong bond formation. Surface morphology showed that the Fe, Cr and O were accumulating on top of matrixes and Fe, Cr, Ni, and O were trying to make bond below this layer which revealed the outer oxide and inner oxide formation, respectively. The strain and defective matrix have shown that the Fe and Cr segregated from the surfaces whereas Ni atom slightly moved to the upper direction, which is similar to the regular matrix. This phenomenon revealed the Ni enrichment at the crack tip region, which is good agreement with experimental results [5]. MSD of oxygen for defective matrix is higher than the regular matrix. It seems that the defective matrix locally oxidized faster than regular matrix. Strain enhanced the diffusivity of adsorbed atom in the matrixes (see Fig. 1). Addition of Cr reduces oxygen atom mobility due to Cr enriched passive film formation in the matrix. Hydrogen atom diffusivity has significantly increased for the defective and strain matrixes in comparison to other matrixes, as shown in Fig. 1. The simulation results made clear that strain plays a role in enhances the dissociation of number of water molecules which lead metal segregation. Figure 2 shows that the diffused hydrogen atoms have negative charge, result is consistent with the previous DFT study [6,7]. These negatively charged hydrogen atoms into matrix oxidized the metallic structure as like as oxygen which weakens the metal atomic bond. Hydrogen atoms diffused deeper in matrixes than the oxygen. As a result, this negatively charged hydrogen atoms work as a oxygen carrier into the matrix [8]. This mechanism enhances the localized oxidation process which increased the metallic solid state oxidation and metal atom bond breakage. This process initiates the cracking of metals.
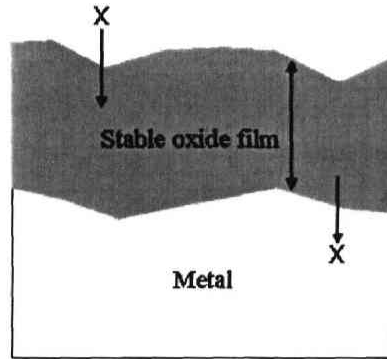
Figure 3 Schematic of SCC resistance alloy.

4 THEORETICAL DESIGN OF SCC RESISTANT Ni-BASED ALLOY

Metallic surface reaction dynamics with defective matrix and strain was discussed in the previous section by considering tight-binding SCF method. This method has been successfully applied to analyze the surface phenomenon of Fe-base atomistic slab model [9]. It has been observed from the tight-binding SCF method that initially water adsorbed on the metal surfaces and dissociated. The dissociated oxygen and hydrogen diffused into matrix and finally oxidized the surfaces. It indicates that the adsorption mechanism is important for understanding the oxidation of metal surfaces. By considering this point, DFT method is another suitable tool which can precisely describe the metal surface adsorption phenomenon. DFT calculation was carried out to better understand the adsorption phenomenon of water molecules, atomic oxygen, and hydrogen in the nickel and chromium substituted nickel matrix. The calculated value revealed that the fcc hollow site is energetically most favorable for oxygen and hydrogen adsorption. The fcc hollow site adsorption energy of 6.15 eV for Ni-Cr matrix was found to be the highest chemisorbed site among all the cases studied here. Atomic charge analysis indicated that the net charge transfer from Ni-Cr matrix to oxygen atom is the maximum. It is found that the on top site is the energetically preferable for water molecule adsorption. Adsorption energy as well as charge analysis indicated the water weakly adsorbed on the metal surfaces and the adsorption was not dissociative. Atomic oxygen remains closer to matrixes in comparison to oxygen of water molecules. The DFT calculations implied that the Ni-Cr matrix is energetically stable for adsorbing atomic oxygen, hydrogen or water molecules in comparison to Ni matrix. The high metal-oxygen bond strength is evidently necessary for the stability of the passive film and the low metal-metal bond strength favors the rapid nucleation and growth of the oxide by facilitating the breaking of the surface metal-metal bonds involved in the early stages of passivation. On this basis, it is believed to be chromium is a passivation promoter. So, surface reactions at the atomic or molecular level understanding may provide the fundamental aspects in oxidation problems, which is very useful for SCC. DFT study revealed that the oxygen makes the strong bond with the metal. Oxygen diffusivity in metal is important for oxidation process. This method has been applied to find suitable elements for the Ni-based alloy, which can form a stable oxide film, as shown in Fig. 3. From the cluster model, Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, Ti, Ce, V, Cr, Pd, and Cu elements have large negative oxidation energies, compared to Ni. This also indicates that the following elements can accelerate the growth of oxide film on metal surface. Hf, Ta, Si, Sc, Ti, Y, Zr, Nb, Rh, W, P, Pd, and Pt elements have high activation energy that implies small oxygen mobility in presence of these elements. Ba, K, Na, Sr, and Zn have a large interatomic bond distance compared to Ni-Ni bond distance. These elements affect on the oxide film protective property as a localized strain. Amongst these elements, Ti, Sc, and Y have high oxidation and activation energies, which satisfy both the requirements. These elements are suitable for the formation of a stable oxide film, as well as possessing small interatomic bond distances compared to Ni. DFT calculations suggested these three elements are favorable for incorporation into Ni-based alloys and another two elements, Hf and Zr, are very competitive. Based on these results, the bulk model has been calculated, with the substitution of these elements into the Ni bulk. The bimetallic bulks (Ti, Sc, and Y) have higher oxidation energies than Ni bulk. The values are consistent with the small cluster model. Mulliken population analysis has shown that the substitute elements have enhanced the electron transfer in both models. Finally, the present calculation recommends that the addition of Ti, Y, or Sc is expected to improve SCC resistance for Ni-base alloy which shows good agreement with experimental study [10-12]. This calculation has been performed, based on the interstitial oxygen effect. For further clarification and confirmation of the result, it is necessary to simulate a large model with different surface oxidation phenomena, as well as performing experiments.

5 CONCLUSIONS

The QCMD have been successfully applied to analyze the SCC phenomenon at the atomistic level. Tight-binding SCF method revealed that hydrogen quickly dissociated and penetrated into matrix. The deeply penetrated negative hydrogen into matrix initiated chemical reaction. The positively charged metal atoms donate excess electron to the deeply diffused hydrogen atoms which initiate the chemical reaction into matrix. Consequently oxygen diffusion into the matrix increased the electron transfer from metallic atom to oxygen which makes attraction in between negatively charged oxygen and positively charged metal atom and the repulsion occur in between metal-metal atom. It has been pointed out that in dealing with complex many electron systems there is generally no single unique way to analyze the bonding. However, the cluster calculations indicated that the transitional metal $4s$ orbitals were most important with some contribution from the $3d$ orbitals [13]. The metal-oxygen electron transfer process helps to form strong bond and finally breakage the ultimate metal-metal bond. The bond breakages indicate the oxidation and formation of oxide layer on the surface. This kind of chemical reaction may take place at the crack tip molecular domain which can assists mass transfer on the regular basis. This process plays a key role in subsequent localized corrosion nucleation like initiation of stress corrosion cracking. On the other hand, DFT revealed that the oxygen made stronger bond with metal. This strong bond may help to reduce the oxygen diffusivity into matrix which can slow down the oxidation process. Based on this point, DFT calculation referred to Ti, Y, and Sc is the best suitable elements among the thirty nine elements which show good agreement with the experimental results. This study provided us fundamental information for the development of expected SCC resistant Ni-base alloy.

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論文審査結果の要旨

　原子力発電プラント用構造材料として使用されている低炭素ステンレス鋼やニッケル基合金では，長期信頼性を損なう応力腐食割れ（Stress Corrosion Cracking: SCC）対策（組成制御）が十分になされてきたと考えられていたが，近年溶接継手部等で SCC が発見され，従来の対策では不完全であることが明らかになっている．そこで，プラントの安全で安心な維持運用には，さらなる SCC 支配メカニズムの科学的合理に基づく解明が不可欠になっている。従来研究の多くは，試験片を用いたき裂進展挙動評価に基づきなされており，き裂先端極近傍のナノ領域における現象解明には至っていない。そこで本研究では，このナノ領域での応力腐食割れ現象の本質解明を目的に，量子分子動力学(QCMD)法を応用してき裂先端近傍における原子レベルでの腐食反応挙動を解析している。特に，水環境中で発生するき裂先端極近傍での腐食現象を支配する，水分子の吸着と解離反応及び解離した酸素と水素の合金内部での拡散挙動，さらにこれらに及ぼすひずみや結晶欠陥の影響を解明したもので，全編 8 章からなる。

　第 1 章は，本研究の背景と目的，本論文の構成を述べている。

　第 2 章では，本解析で用いる QCMD 法で最も重要な，合金を構成する任意の元素間の原子間ポテンシャルを第一原理に基づく密度汎関数法(DFT)解析結果に基づき決定するとともに，そのポテンシャルを用いて解析した材料物性と基礎実験結果と比較することで，設定したポテンシャルの妥当性を検証している．これは本研究手法の実用性を示すもので，工学上重要な知見である。

　第 3 章では，QCMD 法を用い，鉄ークロムーニッケル合金の完全結晶の酸化挙動を解析し，クロム富化表面酸化物形成メカニズムを原子レベルで明らかにしている。また，合金表面で水が解離して発生した水素が合金中へ拡散するとともに，負に帯電して酸化種として振舞うことを世界に先駆けて明らかにしている。これは，水分子による酸化挙動解明に新たな学術的解釈をもたらす工学上極めて重要な知見である。

　第 4 章では，ひずみあるいは表面格子欠陥を導入した結晶中の上述した酸素及び水素の拡散現象を解析しており，酸素及び水素の合金中拡散はひずみや格子欠陥の存在により著しく加速されること明らかにしている。特にひずみの存在は，水分子の解離を助長させるとともに，金属原子からの電子の放出を加速し，結果として酸化の進行を加速することを明らかにしている。これは，酸化反応のひずみ依存性を解明した工学上重要な成果である。

　第 5 章では，DFT 法を用い吸収エネルギーの観点から，ニッケルークロム合金中での酸素及び水素の分布について解析しており，腐食反応中の酸素原子及び水素原子の分布域を示している。本結果は，従来報告されていた実験結果を原子レベルで説明したもので，本研究の解析手法の妥当性を示している。

　第 6 章では，酸化物形成エネルギー及び酸素拡散の活性化エネルギーの観点から QCMD 法を応用して耐 SCC 性に優れたニッケル基合金の設計の設計を行っている。その結果，酸化物形成エネルギーが負で大きく，活性化エネルギーが正で大きい元素として，Sc, Ti, 及び Y 元素の添加が耐 SCC 特性向上に有効であることを提案している。これは工学応用上極めて重要な知見である。

　第 7 章では，合金中の水素元素の SCC 助長メカニズムを体系的に整理し，論じている。これは今後の高信頼材料開発あるいは高信頼原子力発電プラント運用，制御法に対する重要な設計指針を与えるものである。

　第 8 章は結論である。

　以上要するに本論文は，原子力発電プラントの構造材料における SCC の発生メカニズムとして，材料中に拡散した水素がき裂先端極近傍における酸化現象に著しい影響を及ぼすことを解明したものである。さらに， Ni 基合金の耐 SCC 特性向上を図る新たな添加元素を解析的に提案しており，機械システムデザイン工学及び損傷許容工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。