Development of Mixed Continuum-Atomic Modeling Approach to Stress Corrosion Cracking Research-Development of Multiscale Modeling Framework-応力腐食割れ研究に対する連続体-原子混合モデリングアプローチの開発-マルチスケールモデリングフレームワークの開発-

氏名	イスマイル ティルトム Ismail TIRTOM
授与学位	博士（工学）
学位授与年月日	平成２０年９月１１日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科(博士課程)機械システムデザイン工学専攻
学位論文題目	Development of Mixed Continuum-Atomic Modeling Approach to Stress Corrosion Cracking Research - Development of Multiscale Modeling Framework - 応力腐食割れ研究に対する連続体-原子混合モデリングアプローチの開発 － マルチスケールモデリングフレームワークの開発 －
指導教員	東北大学准教授　小川　和洋
論文審査委員	主査　東北大学教授　庄子　哲雄　東北大学教授　坂　真澄 東北大学教授　久保　百司　東北大学准教授　小川　和洋

論文内容要旨

General scope of this thesis is that to link between essential mechanism of stress corrosion cracking (SCC) and plant component behavior by computational multiscale modeling.

Stress corrosion cracking, which is one of the major reason for out-off service condition of nuclear power plants, has been investigated by multiscale modeling. SCC is the cracking induced from the combined influence of tensile stress and a corrosive environment. Therefore, SCC can be defined as localized and accelerated oxidation process under the stress. In this study, we investigated the dynamics of the initial stage of that localized and accelerated oxidation, which is an essential mechanism, at atomic level with the integrated far-field macro stress affect by combining larger scales computational modeling methods (quasi-continuum and finite element methods) with the quantum chemical molecular dynamics method (QCMD) which can simulate the chemical reaction dynamics by considering the electrons interacting with each other and with atomic nuclei. Thesis completed with the explanation of atomistic/continuum combination code and particular characteristics of computational framework for SCC.

1. Introduction

Important aspects of stress corrosion cracking (SCC) problem, summarizing the related studies and objective of this thesis are given in this section. SCC problem mostly appears in the light water nuclear power plants parts, which are in contact with the high temperature water (288 ℃ for boiling water reactors (BWR), and 325 ℃ for pressurized water reactors (PWR)). Such as primary loop recirculation pipes, core shrouds, pressure vessels, steam generators, etc. SCC, i.e., environmentally assisted cracking (EAC) is one of the major causes of out-of-service condition for plants and components. SCC may occur under service conditions, often with no warning, in catastrophic failure. Although SCC is relatively rare, failures can be very costly and destructive when they do occur. The appearance of degradation in components in an operating plant might result in its shut down for repair or replacement of degraded components. It is a worldwide concern that the requirement to replace components puts an economic burden on utilities and their customers. EAC usually occurs after a long incubation time. In spite of a comparatively large research effort in the area, actual EAC mechanisms are not clearly known. Hence, a fundamental understanding of EAC and application of that understanding to predictive models are vital for the technological development and improvement of the reliability of components of in-service plants. In details, the chemical reaction behavior of bare metal surface at crack tip such as anodic dissolution and formation of oxide or protective film is important process for crack propagation. Therefore, understanding the interaction of water with iron or nickel based structural materials and the mechanism of subsequent corrosion on the surface is of fundamental interest to the understanding of EAC behavior.

Since SCC involves a wide range of parameters including mechanical, chemical and metallurgical data, it is extremely difficult to investigate in detail all of these numerous factors by experimental methods. Numerical analysis technique, namely computer simulation of SCC, therefore plays a major role in

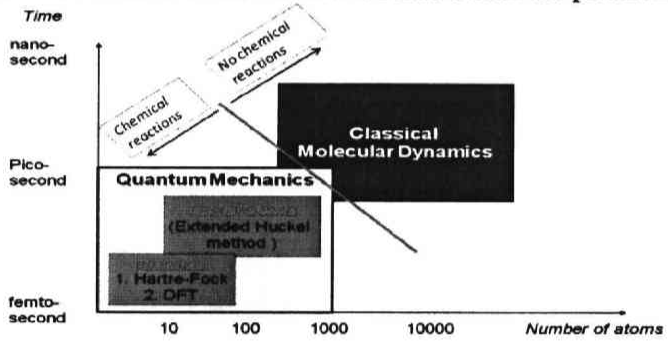
improving the predictive capability of the EAC. Although there are different numerical methods works on different scales, complex nature of SCC, from atomic to continuum, make it necessary to use combination of these different modeling methods.

2. Variations of Size Scale of Microstructure Considered in This Work

This and next chapters establishes strong basis before advancing the further parts by explaining studied various material size scales and modeling methods related to those different scales. The mechanical deformation and failure of many engineering materials are inherently multiscale phenomena in that the observed macroscopic material behavior is governed by processes that occur on many different length and timescales. Material structures can be observed in different ranges, from electron to structural component. The basics of variations of size scale of microstructure considered in this work explained in this section.

3. Multiscale Modeling

Because the accelerated and localized oxidation, as the essential mechanism of SCC, is a chemical process occurs at the very small sizes, order of nanometer scales, atomic level investigation becomes indispensable. Therefore, atomic simulation methods, which recently become one of the major tools in material research, are the most convenient for investigation SCC mechanism. However, atomic modeling methods give us more concrete results, which cannot be obtained by the continuum methods, even classical molecular dynamics methods with very simple potentials are still limited to simulating on the order of 10^6-10^8 atoms for a few nanoseconds. However, real materials are composed of ~10^{23} atoms and molecules hence it becomes necessary to perform atomic simulations integrated with far-larger-scale simulations. Additionally, to simulate oxidation, it is necessary to consider electronic interactions. Basically, two types of methods can calculate electronic interactions at atomic level. Well known ab inito methods, which is not necessary to use any empirical parameter, gives most accurate results about 10-100 atoms at the ground level. Therefore temperature effect is not considering. One scale step up methods are called as tight binding molecular dynamics (TBMD or QCMD) can consider 100-1000 atoms at elevated temperatures. Because of this length and time scale limitation, atomic level methods must be used in conjunction with the surrounding upper level materials modeling methods. The researches for bring together different computational methods are called as multiscale modeling methods. Several methods have been developed for the multiscale simulations. The selection of the method is related with the problem at the hand.



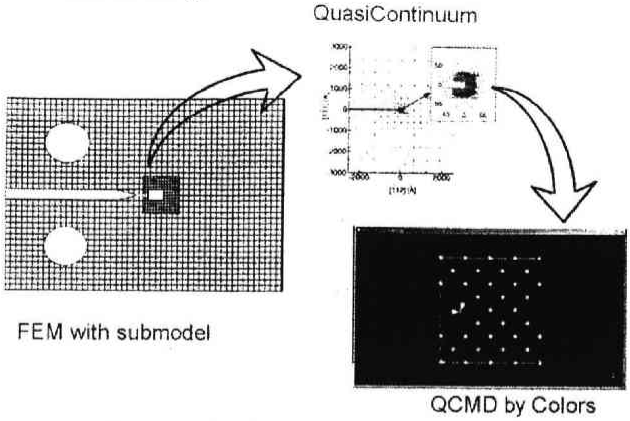
The limits of quantum and classical molecular dynamics methods

4. FEM-QC method-QCMD model for SCC

Construction strategy of our multiscale model is explained. There are a few attempts to connect different scale material modeling methods for oxidation. Target material is generally Si, and Ni or Al single metals. None of the available multiscale methods satisfy our desires for enhanced oxidation at elevated temperatures. Therefore, an efficient multiscale approach has been designed in this study and applied to the Ni-Cr austenitic alloy system. Environmental effect has been ensured by the water molecules interaction with alloy.

Simulation of the stress enhanced oxidation in alloys is a challenging task. Because oxidation is simply an electron transfer process, electronic structure analysis under the loading must be conducted. However there are simulation studies of oxidation of single metal at atomic level, there is no study on solid state oxidation mechanism at atomic level on austenitic steels. In this study, Ni-Cr alloy oxidation simulation has been conducted by Colors QCMD code developed at the Tohoku University. Although we can now simulate the solid state oxidation of austenitic system, it is still a big problem to make the localized and accelerated oxidation simulations because of the integrity of macroscale effects with the studied atomic

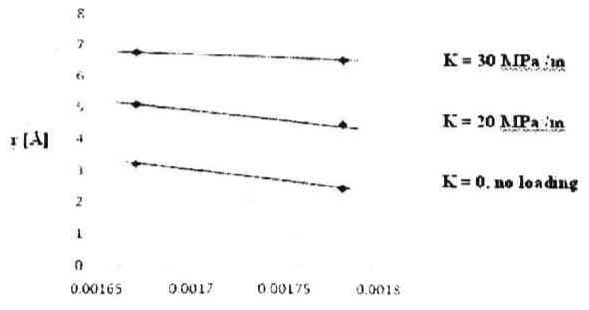
system. Therefore, it is constructed a multiscale modeling technique which composed of FEM, Quasi-Continuum (QC) method and QCMD. With this technique, it is possible to simulate electronic interactions of atoms under the far-field loading effect.



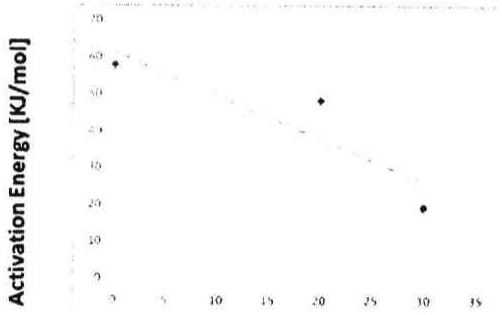
Computational multiscale model for SCC

5. Initial Stage of SCC "Stress Enhanced Oxidation" Simulation by Multiscale Modeling

It is explained the relation between atomic scale phenomenon of oxygen atom diffusion and macroscopic external loading parameter, K using the explained multiscale model. Among the various mechanisms for SCC in high temperature water environments, the enhanced oxidation at the crack tip is generally accepted as a working mechanism, even though the description of the detailed element processes varies in these proposed mechanisms. Therefore, essential mechanism of SCC is that localized and accelerated oxidation. One of the outstanding problems in theoretical lifetime prediction is to understand the mechanism of this oxidation. The factors of making the oxidation localization and acceleration can be classify as mechanical, material and chemical based factors. Among all the factors, macroscale stress and crack geometry as mechanical, grain boundary as material and water and temperature as chemical related factors have been studied in this work. This work provides a multi-scale combination of FEM, Quasi-continuum and quantum chemical molecular dynamics, which made it possible to obtain the K dependence of activation energy of oxygen diffusion in Ni-Cr alloy. Obtained results show that, initial stage of the oxidation is highly affected by the far-field mechanical loading and temperature. Oxygen diffusivity is increasing with both increasing loading and temperature. Computational modeling results of the experimentally unattainable problems help us to understand the underlying mechanisms and show the better ways and new aspects for onward experiments.



Maximum penetration dept of Oxygen vs 1/Temperature



Activation Energy [KJ/mol] vs. Stress Intensity [MPa√m]

The initial stage oxidation behavior is not clearly known. And, there is very few experimental data at the studied temperatures of this work. Therefore, the results are important to give insight onto these unknown regimes. Multiscale simulation results show that, initial stage of the oxidation is highly affected by the far-field mechanical loading and temperature. Oxygen diffusivity is increasing with increasing both loading and temperature. Computational modeling results of the experimentally unattainable problems help us to understand the underlying mechanisms and show the better and new directions for the onward experiments.

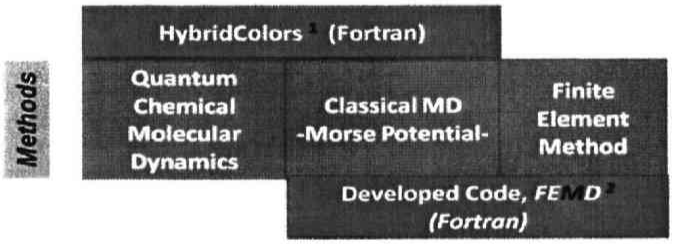
The equation obtained here as

$Qa = Q_0 - \alpha \cdot K$

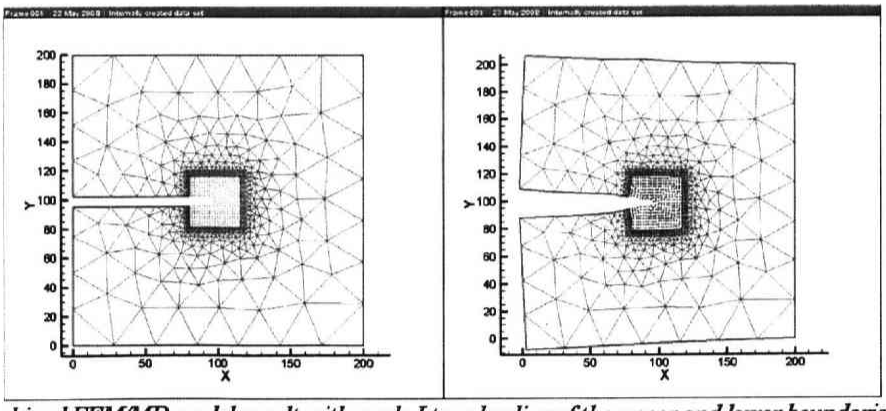
is clearly making a bridge between atomic scale phenomenon of oxygen atom diffusion and macroscopic external loading parameter, K. This kind of equation has been suggested in fracture, plastic deformation and creep but never obtained in oxygen diffusion around 300 °C because of very slow process to measure experimentally. This work provide a multi-scale combination of FEM, Quasi-continuum and molecular dynamics and quantum chemical molecular dynamics, which made it possible to obtain the K dependence of activation energy of oxygen diffusion in Ni-Cr alloy.

6. Coupling of FEM and MD

Here it is described the multiscale code development which's application target is the SCC problem. Only hundreds or thousands of atoms can be solved by quantum description methods such as ab initio MD or Quantum Chemical MD/Tight Binding MD. Therefore it becomes indispensable to couple quantum mechanics with less expensive molecular mechanics or continuum mechanics methods for further applications of SCC. HybridColors, as a combination of TBMD and classical MD has already been developed at Tohoku University. It is developed combination code of classical MD and FEM to integrate it with the HybridColors to enhance its capability.



Combination of QCMD/MD is developed called as HybridColors at Tohoku University. In this work, MD/FEM combination is completed, called as FEMD.



Developed combined FEM/MD model result with mode I type loading of the upper and lower boundaries of FEM part.

7. Development of Modeling Framework for SCC

Scientists develop computational models to predict the SCC mechanisms or further crack growth rate behavior of LWR materials. Promising progresses have been made in modeling material structures at different scales. However, significant challenges in theory and numerical algorithm developments still remain to be overcome. In this part, the particular characteristic of the integrated multiscale modeling framework to overcome all the barriers on the multiscale modeling of SCC has been explained.

8. Conclusions

Our multiscale modeling study showed that, stress affect the oxidation behavior, with the increasing stress, oxygen can more easily penetrate because it will be easier to pass over the decreased activation energy barrier. Obtained results have the big importance because the relation of parameters from very far scale has been proved. The relation of macro stress effect by stress intensity and activation energy of atomic resolution oxidation dynamics.

論文審査結果の要旨

軽水炉においては，構造材料の溶接部等で応力腐食割れ（Stress Corrosion Cracking: SCC）の発生が危惧されており，発電プラントの安全で安心な維持運用には，SCC 発生の詳細メカニズムの解明は不可欠となっている。SCC 現象の本質理解には，き裂先端極近傍で発生している化学反応（酸化）と原子結合の破壊の連成現象を解明することが必須課題となっているが，現状の実験分析技術では実際の高温高圧環境におけるナノスケールでのこのような現象観察は極めて困難である。そこで本論文は，SCC を局在化した加速固相酸化を伴う原子結合の破壊現象であると位置付け，巨視的な応力が作用した際のき裂先端極近傍の酸化挙動と原子結合の破壊を解析できる，原子レベル解析と従来の有限要素法解析を統合した新しいマルチスケール解析技術の確立を目的としている。従来の古典分子動力学（MD）と有限要素法を統合したマルチスケールシミュレーションでは解析できなかった，き裂先端極近傍での原子レベルでの応力依存の化学反応解析を可能とするため，新たに量子分子動力学解析手法を加え，マルチフィジックス解析を可能とする新たなマルチスケール解析技術のフレームワークを提案し，その有効性を示したものであり全編 8 章からなる。

第 1 章は序論であり，SCC 現象解明への課題と既往の研究紹介，本研究の目的と構成について述べている。

第 2 章では，本研究の対象である，き裂先端極近傍での原子レベルでの応力依存の化学反応解析を実現するための研究及び評価方法について基本的な考え方を述べ，併せて化学変化を伴う現象を量子分子動力学（QCMD）で解析し有限要素法(FEM)と結び付ける解析の必要性を示している。これは本研究の基本概念をまとめた重要な成果である。

第 3 章では，原子レベルの解析を行う QCMD と巨視レベルの解析を行う FEM 解析，及び QCMD と FEM を繋ぐメゾレベルにおけるモデリング法について詳述している。これは，本研究で提案するマルチスケール解析技術のフレームワークの根幹をなすマルチスケールモデリング手法であり，工学的に重要な成果である。

第 4 章では，マルチスケールモデリング法として，従来にはない量子分子動力学－古典分子動力学－有限要素解析を統合解析する手法を提案し，巨視的な応力が作用しき裂先端極近傍における局所的な酸化が関与する SCC 現象を解析する手法を確立している。これは，SCC 現象を原子レベルから巨視レベル領域まで一貫して解析する画期的な手法である。

第 5 章では，前章で確立した手法を駆使して軽水炉用構造材料の強度試験における巨視的な応力拡大係数 K とき裂先端極近傍における原子レベルの酸素拡散の相関性を解析し，Ni-Cr 合金における酸素拡散の活性化エネルギーが，き裂先端の応力集中場に強く依存して K 値の増加とともに著しく低下することを明らかにし，その K 依存性を線形近似式で示している。本結果は，速度反応論における活性化エネルギーの K 値依存性の存在を解明した画期的な成果である。

第 6 章では，本研究で提案した QCMD と MD 及び FEM 解析を統合するためのカップリング精度の評価アルゴリズムを提案し，その評価指数の高い独自の統合プログラムの開発を行っている。これにより，原子レベルでの挙動解析技術とマクロな挙動解析技術を統合する方法論を確立している。これは工学の発展に大きく寄与する優れた成果である。

第 7 章では，以上開発したマルチスケール，マルチフィジックス解析技術を総括し，SCC 現象解明のためのマルチスケールモデリングのフレームワークに関する提案をまとめている。これは，今後の SCC 解明研究における理論解析を推進するためのモデリングの基盤となるもので，工学の今後の発展に大きく貢献する成果である。

第 8 章は結論である。

以上要するに本論文は，実験では取り扱うことが極めて困難なき裂先端極近傍の原子レベルにおける応力依存の化学反応現象を解明するために，量子分子動力学－古典分子動力学－有限要素解析を統合したマルチスケール・マルチフィジックス解析を実現するモデリング手法を開発したものである。さらに本手法を用いて，軽水炉材料の応力腐食割れ現象におけるき裂先端極近傍での酸素拡散の活性化エネルギーの巨視的な応力拡大係数 K 依存性を世界で初めて解明しており，機械システムデザイン工学及び損傷許容工学へ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。