氏名	おおみ　としひと 大見　敏仁
授与学位	博士（工学）
学位授与年月日	平成２２年　３月２５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）ナノメカニクス専攻
学位論文題目	The Effect of Stress Rate on Hydrogen Concentration Around a Crack Tip and its Mechanical Control for Steels （鋼材におけるき裂先端近傍の水素凝集挙動に及ぼす応力速度効果とその力学的制御）
指導教員	東北大学教授　横堀　壽光
論文審査委員	主査　東北大学教授　横堀　壽光　東北大学教授　坂　真澄 東北大学教授　三浦　英生　東北大学准教授　杉浦　隆次

論文内容要旨

The research of hydrogen embrittlement has been progressed remarkably in resent year. However, the mechanism of hydrogen embrittlement has not been clarified yet. This may be due to the difficulty of experimental detection of hydrogen distribution since hydrogen is feasible to diffuse in metals.

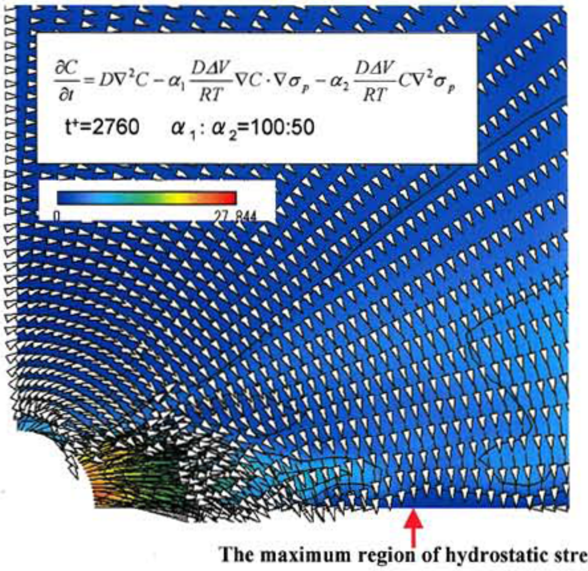
Many of these researches are limited to the clarification in each case of embrittlement mechanism for various materials and under various environmental conditions. Therefore, a unified theory of hydrogen embrittlement mechanism has not been proposed, and many hypotheses of the mechanism of hydrogen embrittlement have been proposed. If these theories are classified roughly, there are two approaches. One is the concept of brittle fracture which a crack preferentially grows along the path where the atomic binding force decreases. The other is that of ductile fracture dominated by plastic deformation. However, concerning hydrogen embrittlement of which the fracture mechanism is different depending on the materials and the environmental conditions, it will be difficult to explain its whole phenomena by one theory.

On the other hand, it is correct that hydrogen embrittlement is caused due to the increase in hydrogen concentration, and it is induced by a small amount of hydrogen such as x p.p.m. to $x\times10$ p.p.m.. If the mechanism of hydrogen concentration behavior which is a dominant factor of hydrogen embrittlement is clarified and the control of hydrogen diffusion becomes feasible, the prevention technique of hydrogen embrittlement can be constructed. However, no research clarifies systematically the mechanism of hydrogen concentration for metals with various mechanical properties and under various temperatures and loading conditions. Furthermore, no research concerns the control method of hydrogen concentration behavior in materials. Therefore, the systematical clarification of the mechanism of hydrogen concentration behavior and the mechanical control of the hydrogen diffusion behavior are effective for prevention of hydrogen embrittlement and control of hydrogen transportation, which is significant from the engineering view point.

However, experimental detection of hydrogen distribution is not feasible due to the high diffusivity of hydrogen in materials. In fact, many methods of detection of hydrogen concentration measure the total amount of hydrogen inflow and outflow from a specimen, and it has not been developed to detect macroscopic distribution of hydrogen and the time sequential characteristic of hydrogen concentration. Under these situations, to obtain the distribution of hydrogen concentration, theoretical analyses have been proceeded. However, it is difficult to solve exactly the equation of hydrogen diffusion and concentration behavior by analytical method. With the improvement of the computer performance, several analyses have been conducted by using numerical methods to obtain the distribution of hydrogen concentration. However, it was not feasible to realize the correct hydrogen concentration behaviors. On the other hand, by using Finite Difference Method (FDM), the α multiplication method proposed by Yokobori et al. enable us to realize stress induced hydrogen concentration by applying the interaction factor, α to the stress induced term. However, when this analysis is applied to the actual structure and various stress conditions, it is necessary to adopt the Finite Element Method (FEM) to conduct local stress analysis which is coupled with FDM for diffusion analysis.

In this study, to prevent of hydrogen embrittlement and to control of hydrogen transport in steels, the mechanisms of hydrogen concentration behavior were clarified and the mechanical control method of hydrogen driving force was proposed. The clarifications of the mechanism on hydrogen concentration behavior under various stress conditions and the fundamental study of the mechanical control method of hydrogen driving force are conducted. The following results and conclusions were obtained in each chapter.

In Chapter 2, concerning the particle diffusion equation with the stress induced driving force, the physical meaning and role of each term of the equation on the particle diffusion behavior were clarified. Since the diffusion equation has been derived to describe physical phenomenon, essentially it is necessary to select α_1 and α_2 , which are multiple parameters of hydrogen diffusion equation, as a reasonable value to adjust the actual natural phenomenon. Therefore, when the effect of local stress gradient on particle diffusion is necessary to be noticed, the second and the third terms are necessary to be multiplied by reasonable values of α_1 and α_2. In the region which is non conservative system such as plastic stress field, since the total amount of particle obtained by the first and second terms decreases with increase in time, it will be necessary to add a little effect of the third term to compensate the decrease in particle. The adding the weight coefficients of α_1 and α_2 to stress induced terms were found to be important to conduct a realistic analysis. Thus, it is important to determine reasonable values of α_i(i=1,2) to relate to the actual phenomenon. Fig.1 shows the hydrogen concentration behavior around a crack tip obtained from the numerical result using the α multiplication method.



The maximum region of hydrostatic stress

Fig.1 Hydrogen concentration behavior at the maximum site of σ_p due to the second term of diffusion equation

Furthermore, the effects of stress rate, stress wave form, yield stress and temperature on hydrogen concentration around a crack tip were systematically analysed and the effect of $C\nabla^2\sigma_p$ on hydrogen concentration was investigated. Under the constant stress rate condition, the hydrogen concentration at the site of elastic-plastic boundary appears remarkably with increase in yield stress and decrease in temperature and stress rate. The dependence of stress rates on hydrogen concentration appears remarkably under the condition of higher yield stress and lower temperature. Under the cyclic loading condition, the hydrogen concentration at the site of elastic-plastic boundary appears remarkably with increase in yield stress and decrease in temperature. Additionally, concerning the effect of the stress wave form on the hydrogen concentration at the site of elastic-plastic boundary, Fast-Slow stress wave form condition was found to promote the hydrogen concentration at the site of elastic-plastic boundary. The third term of the basic equation was found to improve quantitatively hydrogen concentration and the analytical results are qualitatively in good agreement with the analytical results without the term of $C \nabla^2 \sigma_p$.

In Chapter 3, a model of numerical analysis considering the effect of the crack growth rate on hydrogen concentration was proposed. The effects of crack growth rate under the inert atmospheric condition on the hydrogen diffusion and concentration behavior were clarified. Furthermore, the precision of the finite difference method of the inert term was investigated. These analyses concern the hydrogen embrittlement mechanism of corrosion fatigue crack growth rate (CFCGR). The hydrogen diffusion equation taking account for the crack growth rate under atmospheric condition was developed based on the concept of diffusion equation under uniform back wind conditions. These analyses were conducted using the center difference method and the up-wind difference method for the inertia term, which is that of crack growth rate.

For the case of the fatigue crack growth rate which is less than a critical crack growth rate ($U_c = 10^{-8}$ m/s), the hydrogen concentration behavior around a crack tip are almost similar as that under a crack growth rate for a statical crack. This results shows that the crack growth rate does not influence the hydrogen diffusion and concentration behaviors under the condition of lower crack growth rate. In the higher yield stress ($\sigma_{ys} \geqq 1000$ MPa), hydrogen concentration at the elastic-plastic boundary appears remarkably at the critical crack growth rate ($U = 10^{-7}$ m/s) and it decreases with increase in the crack growth rate. The effect of fatigue stress wave form on hydrogen diffusion and concentration behavior appears at the lower crack growth rate. This effect is the same as the case of a statical crack and its effect becomes smaller with increase in the crack growth rate. These results obtained in this chapter were characterized as an effect of dynamics of crack on hydrogen concentration behavior around a crack tip.

In Chapter 4, by using FEM and FDM coupled method, the analyses of hydrogen diffusion were conducted under constant stress and cyclic loading conditions. On the basis of this analysis, the effect of the re-yielding region on hydrogen concentration under cyclic loading condition was clarified. Furthermore, the controllable feasibility of hydrogen concentration behavior due to the stress induced driving force was proposed. Under the constant stress condition, results of hydrogen concentration behaviors obtained by this method were found to be similar as those obtained by the analyses using analytical solutions of the elastic-plastic stress field around a crack tip. Under cyclic loading condition, the analyses of hydrogen diffusion and concentration behavior considering the effects of yielding and the re-yielding region were conducted. Fig.2 shows the hydrogen concentration behavior around a crack tip

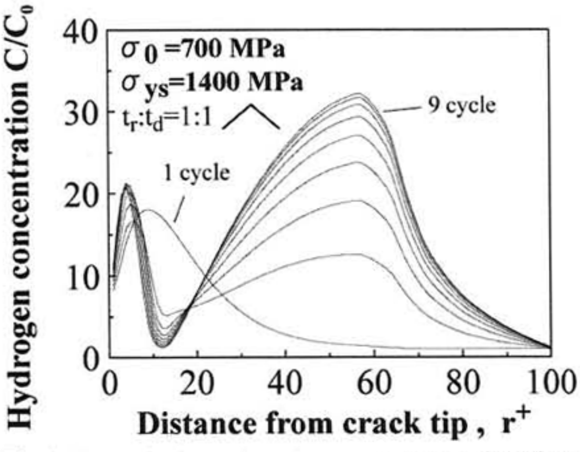


Fig.2 Numerical results of hydrogen concentration at the initial yield and the re-yield region under cyclic loading

under cyclic loading condition. Due to the effect of the re-yielding region on hydrogen concentration behavior under cyclic loading condition, hydrogen was found to accumulate at both of the elastic-plastic boundary in the first loading process and of the real elastic-plastic boundary caused by re-yielding under cyclic load condition. FEM-FDM coupling analyses based on the α multiplication method enable us to obtain those characteristics of hydrogen concentration behaviors. The effects of stress wave form on hydrogen flux were analyzed under cyclic loading condition by FEM-FDM coupling analysis. The hydrogen flux was found to be larger under Fast-Slow stress wave form condition and smaller under Slow-Fast stress wave form condition. The effects of stress wave form on the hydrogen flux appear remarkably with increase in higher yield stress. On the basis of the analytical result which show the difference in the stress induced hydrogen driving force due to the stress wave form, the controllable feasibility of hydrogen flow under cyclic loading condition was proposed.

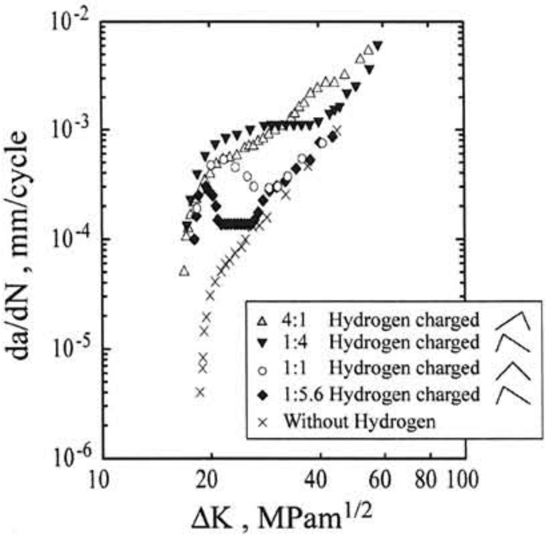


Fig.3 The experimental result of FCGR of a specimen with hydrogen charge under atmospheric condition

In Chapter 5, on the basis of the analyses of hydrogen diffusion and concentration behavior, the mechanical controllability of hydrogen concentration or flowing out was proposed which is aimed to apply to the test method of hydrogen embrittlement using a small specimen. There are two cases of hydrogen concentration in a specimen and flowing out from a specimen due to the competitive effect of gradients of hydrogen concentration and stress distribution. On the basis of this result, the test method which enables to conduct hydrogen embrittlement test using a small specimen under atmospheric condition is proposed by mechanically accumulating hydrogen in a specimen. In hydrogen embrittlement test using a small specimen under atmospheric condition, the acceleration of fatigue crack growth rate (FCGR) of a specimen with hydrogen charge was realized and it was considered to be caused by hydrogen embrittlement. Experimental result of FCGR is shown in Fig.3. This result shows that the validity of using a small specimen under atmospheric condition by adopting the method of hydrogen charge under sustained load for the notched specimen. Plateau regions of crack growth rate appeared under Fast-Slow stress wave form condition. In these regions, intergranular fractures were observed. On the other hand, the plateau region of crack growth rate was not obtained under Slow-Fast stress wave form condition. These results show that the crack growth mechanism under Slow-Fast stress wave form condition is different from that under Fast-Slow stress wave form condition. This will be due to the difference in hydrogen distribution around a crack tip between under Fast-Slow and Slow-Fast stress wave form conditions. The latter show the higher hydrogen concentration around a crack tip and it causes the mechanical interaction with dislocations which results in facet like fracture.

In Chapter 6, the concluding remarks were conducted.

論文審査結果の要旨

鋼材における水素脆化のメカニズム解明は，工学的に重要課題であるにも関わらず未だに十分になされていない。これは水素脆化の主たる要因である材料中の水素凝集挙動を明らかにする解析および実験方法が確立されていないことに因る。著者は，新たな数値解析法と水素脆化試験法を提案し，き裂先端近傍の水素凝集挙動に及ぼす応力速度効果を明らかにし，水素輸送制御手法に関する基礎基盤的知見を得ている。本論文は，これらの研究成果をまとめたものであり，全編6章からなる。

第1章は緒論であり，本研究の背景および目的と意義について述べている。

第2章では，応力誘起物質輸送論として記述される水素拡散方程式に関して考察を行って問題点を明示し，合理的な水素凝集挙動解析を可能とする解析手法を提案している。また，この手法を用いてき裂先端近傍における水素拡散凝集挙動解析を系統的に行い，水素凝集挙動に及ぼす応力速度効果，負荷応力波形効果，降伏応力効果および温度効果を明らかにし，従来の解析手法による結果との比較検討を行い，その有効性を検証している。本結果は，水素凝集挙動を予測するための数値解析を行う上での重要な知見であり，工学的に有用な成果である。

第3章では，水素凝集挙動に及ぼす大気中の疲労き裂成長速度の効果を，静止したき裂の周りで解析空間が一定の速度で運動する拡散解析問題として解析し，き裂成長速度に水素脆化を促進する臨界値が存在することを見出している。この結果は実験結果と定量的にも一致し，水素脆化によるき裂成長の予測にとって有効かつ重要な知見である。

第4章では，より複雑な応力場における水素拡散凝集挙動を解析することを目的に，FEM-FDM連成解析手法を構築し，疲労条件下における再降伏領域を考慮した水素拡散解析を行い，水素凝集挙動に及ぼす再降伏領域の影響について明らかにしている。本結果は，き裂先端近傍での水素駆動力に負荷応力波形効果が影響することを示し，水素輸送の可制御性を解析的に示す重要な知見である。

第5章では，水素拡散凝集解析から大型試験片を用いた水素脆化試験法の妥当性を示している。また，この結果を応用して，応力負荷環境で水素チャージを行うことにより，小型試験片を用いても大気中での水素脆化試験が可能となる方法を提案し，実験により本手法の有効性を実証している。本結果は，水素脆化試験法の発展にとり重要な成果である。

第6章は結論である。

以上要するに本論文は，水素凝集挙動を予測するための数値解析手法を確立して水素凝集挙動に及ぼす力学的効果を明らかにするとともに，水素輸送の可制御性も理論・実験の両面から実証したものである。ここで得られた成果は，水素脆化メカニズムの解明と水素脆化の防止に有益なものであり，ナノメカニクスおよび機械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。