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研究課題名(和文) Real-time quantitatively assessing the corrosion-induced hydrogen trapping in metals

研究課題名(英文) Real-time quantitatively assessing the corrosion-induced hydrogen trapping in metals

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研究成果の概要(和文)：この助成プロジェクトの研究期間中、JIM、JSNDI、JSCE、EuroCorr、IAESを含む専門学会で10件の口頭講演が行われた。1つの特許は出願準備中で、3つの定期刊行物論文が提出され、審査中である。

研究成果の学術的意義や社会的意義

The output of this study will not only provide significant clues for designing stronger alloys against environmental degradation and corrosion, but also establish a database for allowing an in-situ and real-time monitoring of the corrosion-induced damage.

研究成果の概要(英文)：Firstly, the main idea of the project was to link corrosion-induced hydrogen ingress into metals and real-time Acoustic Emission (AE) signals, but unfortunately proved to be "negative" according to the experimental data obtained so far. In the future, more investigation with improved framework will be conducted to further verify this original idea. On the other hand, thanks to this grant funding, one experimental framework, i.e., micro-electrochemical system equipped with in-situ high-speed microscopy and real-time AE monitoring, was successfully established; And one original electrochemical test approach, i.e., intermittent anodic polarization (IAP) test approach, was developed.

During the study period of this grant project, 10 oral presentations were published in the professional societies including JIM, JSNDI, JSCE, EuroCorr, and IAES. One patent is being prepared for application and three journal papers were submitted and under review.

研究分野：材料加工および組織制御関連

キーワード：localized corrosion SCC hydrogen evolution X-ray CT acoustic emission TDS steels

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1 . 研究開始当初の背景 (Background)

In 1875, Johnson described “remarkable changes produced in iron by the action of hydrogen and acids” [1]. Since then hydrogen-induced damage phenomena termed as hydrogen embrittlement (HE) to metallic alloys have been widely recognized. The type of HE largely depends on the source of hydrogen. The corrosion reaction is one typical case in which corrosion-induced hydrogen often leads to the delayed brittle fracture which depends directly on the trapped hydrogen content. Since this type of failure involves time for the diffusion of hydrogen, a real-time assessment of the hydrogen content during the incubation period would be of great significance in predicting the crack initiation. Whereas, measurement of hydrogen content in materials still remains a difficult problem because hydrogen is notorious for its dynamic, small-size and hard-to-detect. To date, the prevailing hydrogen characterization methods include the glycerin method (GM), inert gas fusion heat conduction method (IGFHCM), thermal desorption spectroscopy method (TDS), secondary ion mass spectroscopy (SIMS), atom probe tomography (APT) and hydrogen micro-print technique (HMT) [2]. The principle of the former three methods is that hydrogen desorption occurs after the samples are heated to some extent; the latter three methods require strict preparations of specimens but determine the very local microscopic hydrogen content. Recently, electrochemical hydrogen permeation technique has attracted attention in estimating trapped hydrogen in steels [3]. However, this method is susceptible to numerous pitfalls in obtaining data. In this proposal, a new idea focusing on the AE response of hydrogen-bubble evolution which goes with hydrogen diffusion during corrosion is put forward to explore a real-time assessment of the hydrogen trapping in metals.

2 . 研究の目的 (Purpose)

The purpose of this study is to explore a real-time assessment of the hydrogen trapping in metals through monitoring the acoustic emission (AE) signals of the concurrent hydrogen bubble evolution during corrosion.

3 . 研究の方法 (Method)

The initiation of corrosion cracking is often determined by processes whose outcome is the result of competition among strain accumulation and/or stress concentration, anodic dissolution, and cathodic hydrogen reactions. For high-strength alloys under neutral NaCl droplet, the hydrogen trapping largely impose the pit-to-crack transition.

- The important reaction related to H source [4] is: $2H^+ + 2e^- \rightarrow 2H_{ad.}$ (Volmer reaction)
- The recombination of adsorbed H releases hydrogen-bubbles: $2H_{ad.} \rightarrow H_2 \uparrow$ (Tafel reaction)
- The absorption of H corresponds to the hydrogen trapping: $H_{ad.} \rightarrow H_{ab.}$ (dissolved)

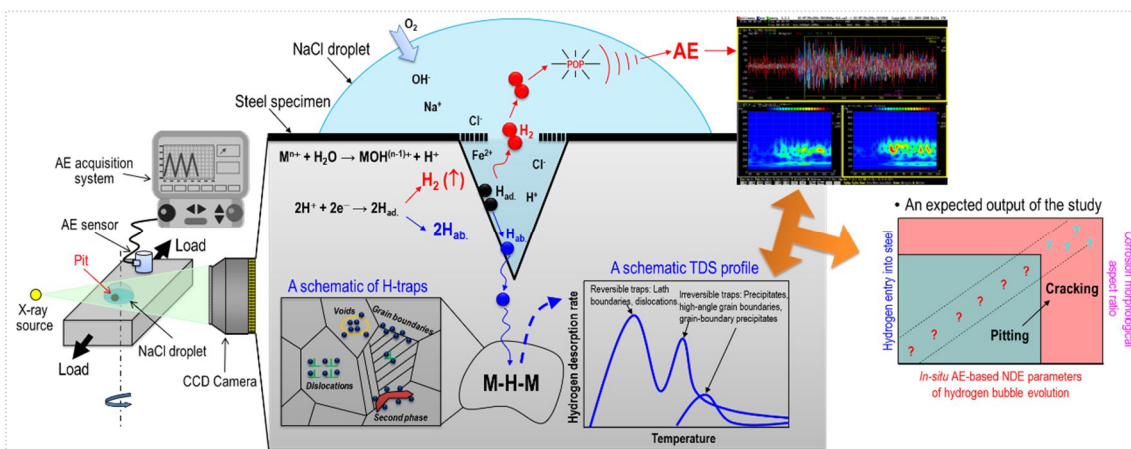


Figure 1 A schematic highlighting the motivation and framework of the proposed study.

Fig. 1 shows the motivation and framework of this proposed study. In this study, the idea is triggered based on a logical assumption that hydrogen bubble evolution is proportional to the hydrogen absorption and trapping. Unlike other methods directly measuring the trapped hydrogen itself, which is inaccessible for the real-time use, this original idea aims at monitoring the concurrent hydrogen bubble evolution with AE to assess the trapped-H content. This method driven by a nondestructive perspective is expected to be with high feasibility in real-time quantitatively assessing the hydrogen trapping and then improving the understanding of HE mechanism.

4. 研究成果 (Results)

According to Figure 2, it has uncovered the pit-to-crack transition by combining the in-situ real-time optic video observation, AE monitoring, finite element analysis (FEA) and XCT scanning. AE method showed high sensitivity to the observed hydrogen bubble evolution and crack initiation. The corrosion evolved from the early localized pitting corrosion, the subsequent H₂ bubble evolution, and the final cracking initiation and propagation prior to the final fracture. Especially the FEM analysis and XCT imaging confirmed that the crack preferentially initiated at the pit bottom whereby the maximum stress concentration occurred. Then, to confirm the hydrogen diffused into the steels during the corrosion process, a serial of tests with the steel specimens of the same preparations was conducted. The tests were interrupted for TDS measurements with reference to the characteristic step of the corrosion evolution, i.e., the early localized pitting corrosion, the pit-to-crack transition, the crack initiation, the crack propagation, and the final fracture. The time points for interrupting the tests were determined based on the real-time optic observation of corrosion evolution and AE signals.

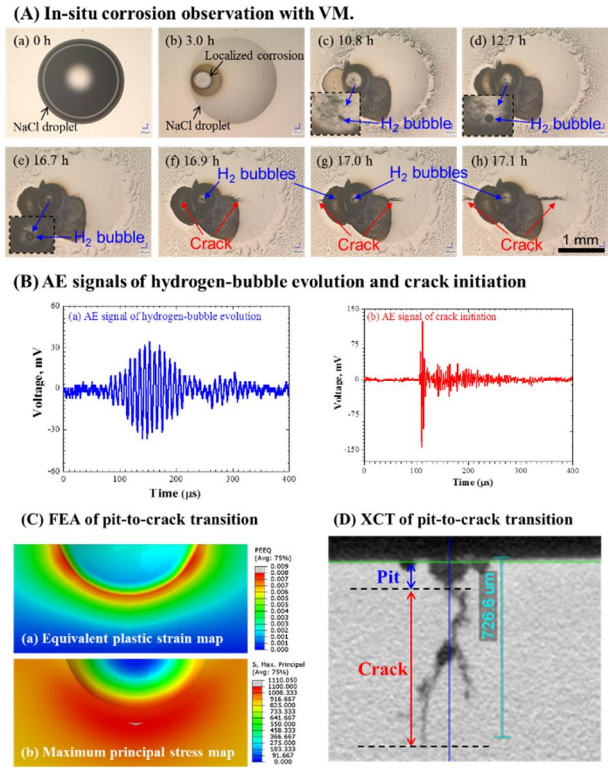


Figure 2 Pit-to-crack transition in a 1.6 GPa-grade 13% Cr SUS402J2 steel under 1.0% NaCl droplet.

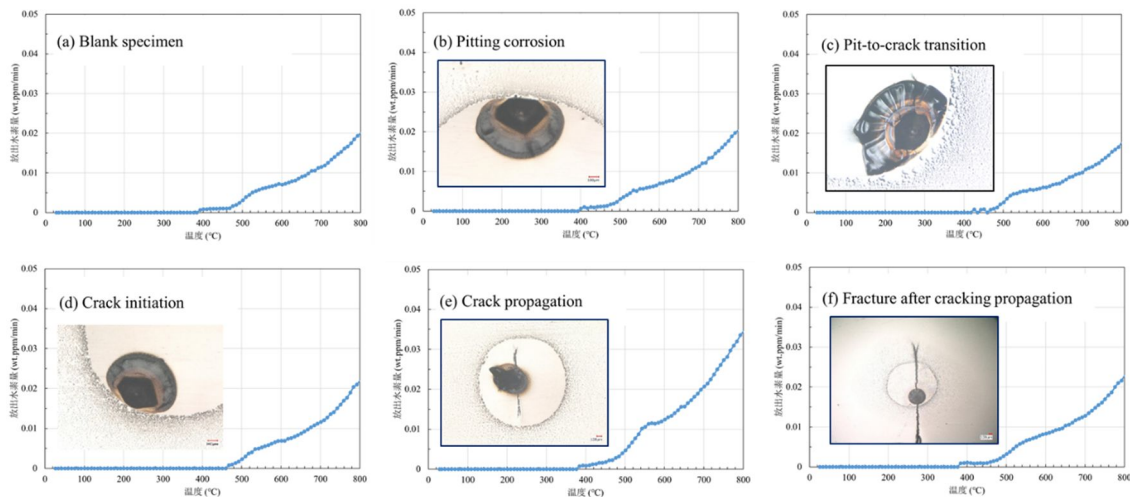


Figure 3 The TDS results of SUS420J2 which were interrupted at different points: (a) Blank specimen; (b) Pitting corrosion; (c) Pit-to-crack transition; (d) Crack initiation; (e) Crack propagation; (f) final fracture.

Figure 3 shows the TDS results from the reference specimen and corroded specimens. Unfortunately, it shows that the diffusible hydrogen content into the steels are almost ZERO based on the TDS curves. This is a NEGATIVE result against the motivation and design of this study. There are two primary reasons accounting for the results.

- (1) The diffusible hydrogen content is essentially low and undetectable in this experimental arrangements.
- (2) The escape of hydrogen trapping in metal occurred during the preparation of TDS samples.

Next, a further framework is being planned to improve the experimental procedure to revalidate the idea of this study, including shortening the time gap between the end of corrosion testing and the start of TDS measurements, adjusting the size and number of salt droplet and strain applied to the specimen surface, validating the feasibility on high-strength Al and Mg alloys.

On the other hand, thanks to the grant funding of this KAKENHI project, an original intermittent anodic polarization (IAP) test approach was developed to study the local microstructures-based localized corrosion. Figure 4 shows the IAP results obtained on $Mg_{89}Zn_4Y_7$ alloy. In detail, immediately interrupting the anodic polarization when it triggered a pit can repassivate this pit. Subsequently, restarting the anodic polarization from the breakdown potential (E_b) of the previous pit caused the initiation of another pit instead of reactivating the passivated pit, which was attributed to the thicker protective oxide corrosion products layer adhered to the pit bottom. The IAP test approach allows a quantitative comparison of localized corrosion susceptibility of local microstructures and an in-situ understanding of localized corrosion mechanisms.

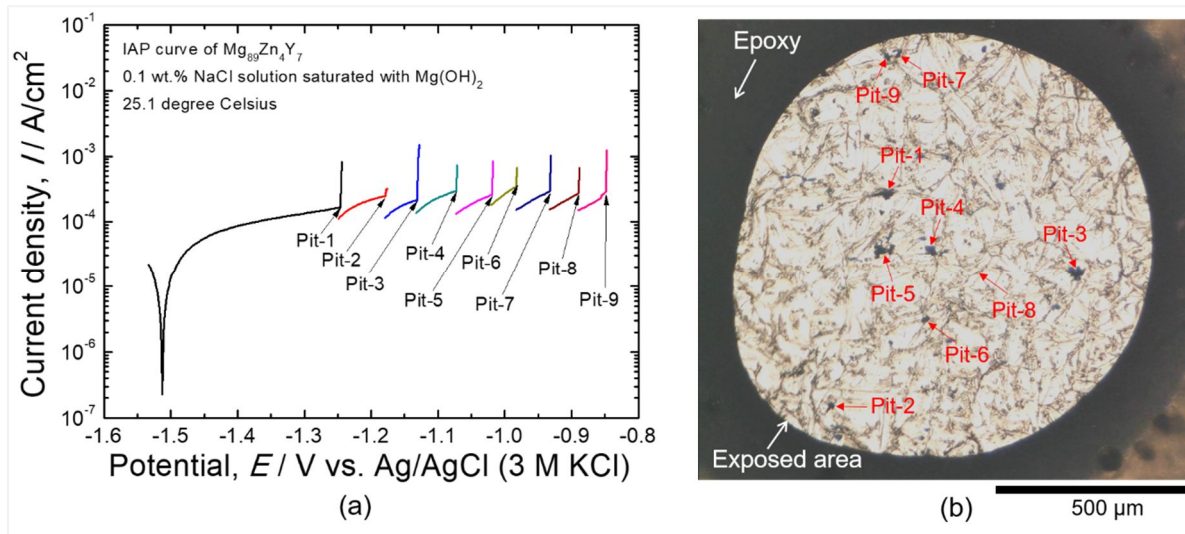


Figure 4 The IAP test of $Mg_{89}Zn_4Y_7$ alloy in 0.1 wt.% NaCl saturated with $Mg(OH)_2$ at room temperature: (a) IAP curve; (b) The surface morphology of the corrosion specimen with all pits that were initiated at different E_b on different traceable local microstructures.

5. 主な発表論文等

〔雑誌論文〕 計0件

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4. 発表年 2023年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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