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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　李　俊燮

学 位 論 文 題 名

Study on Degradation of Passive Film Formed on Stainless Steels by Anion-generating System
（アニオン発生システムによるステンレス鋼不働態皮膜の劣化に関する研究）

Stainless steels suffer from localized corrosion in aqueous solution containing chloride ions. Localized corrosion of stainless steel is strongly dependent on concentration of aggressive chloride ions breaking down the passive film and degradation behavior of passive film on stainless steel. The presence of MnS inclusions in stainless steel provides localized corrosion sites. It is considered that the passive film near MnS inclusion is degraded due to some S species released from the inclusion and initiates the localized corrosion. The localized corrosion process of stainless steel is ordered as a sequence of i) stability-change in passive film, ii) initiation of the passive film, and iii) propagation of localized corrosion. The initial stability-change in passive film is regarded as an important process in the localized corrosion. Though the propagation process is contemplated as a function of concentration of chloride ions and pH in damaged morphology of bare surface of stainless steel, the role of hydrogen sulfide ions, one of primal S species, for stability-change in passive film has not been cleared. Since corrosion reaction is an electrochemical phenomenon, electrochemical techniques are effective to investigate localized corrosion. However, it is difficult to find out the site where the localized corrosion initiates and to record the process how the corrosion initiates at the one site. The development of a state-of-the-art experimental technique and application to investigate the role of aggressive anions for localized corrosion are expected.
In this thesis, two anion generation systems (liquid-phase ion guns, LPIGs) were developed and applied to study degradation of passive film on stainless steels. The system successfully generated sulfide ions or chloride ions in aqueous solution with a maximum concentration of 10^{-2} mol dm^{-3} in the vicinity of specimen surface. Using LPIG, change in stability of passive film, initiation and/or propagation of localized corrosion, and local corrosion resistance of stainless steel were investigated.

In the Chapter 1, previous knowledge concerning stainless steel, passivity and passivity breakdown were reviewed. The purpose of this thesis was also introduced.
Chapter 2 presented experimental setups used in this thesis.
In Chapter 3, LPIG, system for generating sulfide ions, was developed using a microelectrode technique and applied to local sulfidation of a silver surface in pH 8.4 boric acid-borate buffer solution. It was confirmed that cathodic polarization of the LPIG microelectrode covered with Ag_2S successfully generated HS^- in pH 8.4 buffer solution. Generation of HS^- from the LPIG was accompanied with equivalent generation of OH^-. Both anions-generation was strongly affected by diffusion of anions to solution bulk. It was expected that this technique is a safe method using sulfide ions and is effective to generate sulfide ions on a local site of substrate.
In Chapter 4, LPIG for generating sulfide ions was applied to investigate a degradation type 316L stainless steel surface in pH 8.4 boric acid-borate buffer solution. Galvanostatic polarization of the LPIG microelectrode generated both HS^- and OH^- above the stainless steel surface. Generation of these anions by LPIG in the vicinity of the stainless steel results in an increase of anodic polarization current flowing through the stainless steel. Electrochemical impedance spectroscopy, Mott-Schottky analysis and scanning electrochemical microscopy revealed that a relatively defective passive film was formed in solution containing HS^- than

that formed in solution containing no HS^-. AES and XPS revealed that the passive film formation accompanied the contamination of sulfide ions from solution containing HS^-. It was suggested that the HS^- adsorbed with high polarizability on the film surface were incorporated in the film and makes the film conductive as donor levels. Change in the stability of the passive film was expected to be a trigger for the initial depassivation of stainless steel in chloride-containing solution.
In the Chapter 5, the LPIG for generating chloride ions was applied to evaluate localized corrosion resistance of type 430, 304 and 443 stainless steels in sulfuric acid and sodium sulfate solutions. Rapid increase in anodic current flowing through stainless steel was observed during potentiostatic polarization of the LPIG microelectrode, corresponding to propagation of localized corrosion on stainless steel due to an enrichment of chloride ions generated from LPIG. The period and electric charge for the initiation of localized corrosion were dependent on pitting resistance equivalent number, PRE, indicating that these parameters obtained from the operation of LPIG became additional parameters for evaluating localized corrosion resistance of stainless steels. Type 443 stainless steel showed a longer period and a larger charge during cathodic polarization of LPIG than other type 430 and 304 stainless steels, suggesting that type 443 was more resistant against localized corrosion than type 430 and 304 stainless steels. AES and TEM-EDS revealed the presence of Cu at the passive film/substrate interface played an important role of superior localized corrosion resistance of type 443 stainless steel than that of type 430 and 304 stainless steels.
The Chapter 6 summarizes this thesis.

The use of LPIG technique was successfully clarified the initial process of degradation of passive film as its stability-change induced by hydrogen sulfide ions and the initiation and/or propagation of localized corrosion. The LPIG generating chloride ions can also be used to evaluate the localized corrosion resistance of stainless steels. The findings about roles of sulfide ions and chloride ions in degradation of passive film through this thesis is expected to contribute a fundamental understanding of localized corrosion of stainless steels and a developing additional model for an initiation of localized corrosion.