Real Time Monitoring of Repassivation to Study the Elementary Steps after Mechanically Induced Depassivation

Most of the technically important metals and alloys can be employed only since they passivate, i.e., they form a thin compact and protective oxide film that is often just a few atomic layers thick. These materials exhibit a high thermodynamic driving force to repassivate. This means that they are able to repair defects in the passive film. Charge and matter transport is necessary only over very short ranges of multiples of atom radii.

The kinetics can be studied electrochemically by a current measurement. This measurement however delivers usually only integral information. In an attempt to study the elementary processes of mechanical disruption in microscopic areas several techniques have been developed or refined. They all have in common a high-speed sensitive current detection system that allows measuring the current 20 million times each second.

To demonstrate the applicability of the system a three body corrosion type was investigated. Particel induced flow corrosion takes place when a small solid particle like a grain of sand or quartz is flushed within a cooling water system or a pump and hits the surface of the tubing. It causes a small local depassivation. An experimental setup was realized that allows the real time detection of a single particle impact. The depassivation time was typically below 10 μs and the resulting depassivation transient could be linked to the mechanical defect from the impact.

The same particles were employed in indenter experiments to perform the destruction under well controlled conditions and to study the exact mechanism of destruction. Not only the mechanical properties of the passive layer are of importance but also these of the underlying material. Some examples shall illustrate that.

Nitinol is a shape memory alloy which exhibits extraordinary mechanical properties such as superplasticity or a shape memory effect. It is used for glasses frames, orthodontic arch wires and coronar stents. A health risk results from the high nickel content of 50 at.% which may cause allergic reactions. Again, a thin passive film mainly formed by the second compound titanium and oxygen prevents further dissolution. Under mechanical loads however small cracks form in the oxide film which can release nickel. This can be studied by means of an in-situ tensile tester that monitors the repassivation during cyclic stretching. This approach aims to support the development of biocompatible surface treatments.

Curriculum Vitae

Name: Achim Walter Hassel
Date of Birth : December 20, 1966
Position and Institution: Head of Research Group, Electrochemistry and Corrosion, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf
Address: Max-Planck-Str. 1, 40237 Düsseldorf, Germany (Tel.: +49-211-6792-464, Fax: -218 E-mail: hassel [at] elchem.de)
Major Research Field: Nanotechnology and Tribocorrosion
Scientific Biography : Chemist, Computer Science by education
June, 1997; PhD Heinrich-Heine-University, Düsseldorf
June 1997; Scientist, Physics Department, HHU, Düsseldorf
October 1997; JSPS PostDoctoral Fellow, Faculty of Engineering, Hokkaido University, Supervisor Prof. Masahiro Seo
October 1999; Head of Research Group Electrochemistry and Corrosion in the Department for Interfacial Chemistry and Surface Technology, Max-Planck-Institut für Eisenforschung, Düsseldorf

Mechanical and Chemical Interactions of Passive Metal Surfaces Evaluated by Nano-indentation or Nano-scratching in Aqueous Solution

The corrosion resistances of metals and alloys are sustained by protective properties of very thin and compact oxide films, i.e., passive films, formed on their surfaces. If the passive films are locally broken down and not repaired, the substrate metals are subjected to localized corrosion such as pitting corrosion. The breakdown and repair of passive films are always situated under mechanical and chemical interactions. The study on mechanical and chemical interactions is called " mechanochemistry". Mechanochemistry, however, is not sufficiently established since there are no reliable tools developed so far to investigate mechanical and chemical interactions. Recent development of nano-indentation and nano-scratching techniques have succeeded in determining the mechanical properties of very thin solid films such as hardness, elastic modulus and friction coefficient..

In this study, nano-indentation or nano-scratching to the iron surfaces electrochemically controlled at passive state in pH 8.4 borate buffer solution was performed to investigate the mechanical properties from the mechanochemical viewpoint. It is known that chromate or dichromate treatment improves the corrosion resistance of iron. The hardness of passive iron surface obtained with nano-indentation in solution was increased by dichromate treatment, which was ascribed to promotion of repassivation due to chromium enrichment in passive film. The results of cyclic nano-indentation to the passive iron surface in the presence of dichromate ions in solution have indicated that hexavalent chromium ions promote the repassivation at the breakdown sites of passive films during nano-indentation. The friction coefficient of the passive iron surface obtained with nano-scratching in solution increased with increasing the formation potential of passive film, which was always larger than that obtained with nano-scratching in air after passivation. The large friction coefficient of passive iron surface obtained with nano-scratching in solution was explained in terms of high repassivation rate assisted by the potential difference. Furthermore, the mechanical properties of passive Ti and Ta surfaces obtained with nano-indentation or nano-scratching in solution will be also discussed from the mechanochemical viewpoint.

Curriculum Vitae

Name: Masahiro Seo
Date of Birth : January 11, 1943
Position and Institution: Professor, Laboratory of Interfacial Electrochemistry, Graduate School of Engineering, Hokkaido University
Address: Kita-13 Jo, Nishi- 8 Chome, Kita-ku, Sapporo 060-8628, Japan (Tel / Fax :+81-11-706-6735, E-mail: seo@elechem1-mc.eng.hokudai.ac.jp)
Major Research Field: Interfacial Electrochemistry and Corrosion Science
Scientific Biography :
March, 1970; Graduated Doctor Course of Applied Chemistry, Faculty of Engineering, Hokkaido University
April, 1970; Research Associate at Faculty of Engineering, Hokkaido University
October, 1976; Associate Professor at Faculty of Engineering, Hokkaido University
April, 1990; Professor at Faculty of Engineering, Hokkaido University
Since April, 1997; Professor at Graduate School of Engineering, Hokkaido University