Effects of pH and Sulfate Ion on the Electronic Properties of the Passive Film on Fe-20Cr-15Ni

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Previous reports on physical and electronic structure of passive films formed on stainless steels in aqueous solutions have diversity depending on the experimental conditions. Especially, pH and composition of the solution, in which passive films are grown, are important factors. It is usually known that passive film formed on stainless steel in neutral solution is composed of (Fe, Cr) mixed oxide, and that in acid solution mainly consist of Cr oxide. Role of Ni was not yet clarified, relatively. Most of the neutral solutions were borate buffer solutions, and most of the acid solutions were sulfuric acid solutions in previous works. Due to this fact, it is unable to clearly distinguish the effects of pH and sulfate ion on the structure and composition of passive film. Therefore, the objective of this study is to investigate the effects of each of pH and sulfate ion on the structure and composition of passive film on stainless steels, respectively, by photoelectrochemical technique and Mott-Schottky analysis.

Borate buffer solution and 0.1 M sulfuric acid solution (0.1 M H_2SO_4 solution mixed with 0.1 M Na_2SO_4 solution) were used in this study. pH of the solution was prepared to be 2 and 4 for both kinds of solutions, and 8.5 only for borate buffer solution.

The photocurrent spectrum for the passive film formed on Fe-20Cr-15Ni in pH 2 ~ 8.5 borate buffer solution consisted of three spectral components, each of which has a peak at about 3.8 eV, 4.5 eV, and 5.7 eV. These photocurrent spectral components are considered to be originated from d-d and p-d transition of γ-Fe_2O_3 and NiO, respectively, based on the previous researches [1-3]. This result indicates that the passive film formed on Fe-20Cr-15Ni in borate buffer solution is composed of Cr-substituted γ-Fe_2O_3 mixed with NiO [3], independently of solution pH. The capacitance behaviors confirmed this conclusion; the Mott-Schottky plots of the passive films formed on Fe-20Cr-15Ni in pH 2 ~ 8.5 borate buffer solutions were almost same in shapes. They exhibited positive slopes above the flat band potentials, demonstrating n-type semiconductivity of γ-Fe_2O_3. The flat band potential was increased from -0.49 V_{SCE} to -0.07 V_{SCE} with decrease in pH. The acceptor density was 3.5×10^{20} cm^{-3} ~ 6.5×10^{20} cm^{-3} and increased with decrease in pH.

For the passive films formed in sulfuric acid, the photocurrent spectral component of NiO was not measured, as Fig. 1 shows. It is presumably because Ni was more actively dissolved in sulfuric acid solution than in borate buffer solution, and/or Ni formed sulfide instead of oxide in sulfuric acid solution. The shapes of Mott-Schottky plots for the passive films formed in sulfuric acid solution were not different from those in borate buffer solution, probably because the base structure (γ-Fe_2O_3) of the passive films is the same and NiO hardly affects the capacitance behavior due to its small amount. The flat band potential of the passive film formed in sulfuric acid was -0.06 V_{SCE} ~ 0 V_{SCE} and slightly higher than that in borate buffer solution. It is considered to result from the change of chemical composition. The acceptor density was 2.1×10^{20} cm^{-3-} ~ 9.1×10^{20} cm^{-3} and decreased with increase in pH, more significantly than in borate buffer solutions.

It can be concluded from this study, that the base structure (Cr-substituted γ-Fe_2O_3) of passive film formed on Fe-20Cr-15Ni is not changed by pH and sulfate ion of solution. However, the composition of the film is considered to be affected by sulfate ion; particularly, it appeared that NiO is rarely formed in the passive film due to the sulfate ion in the solution. And, the flat band potential and acceptor density was higher in the solution with sulfate ion and lower pH.

References

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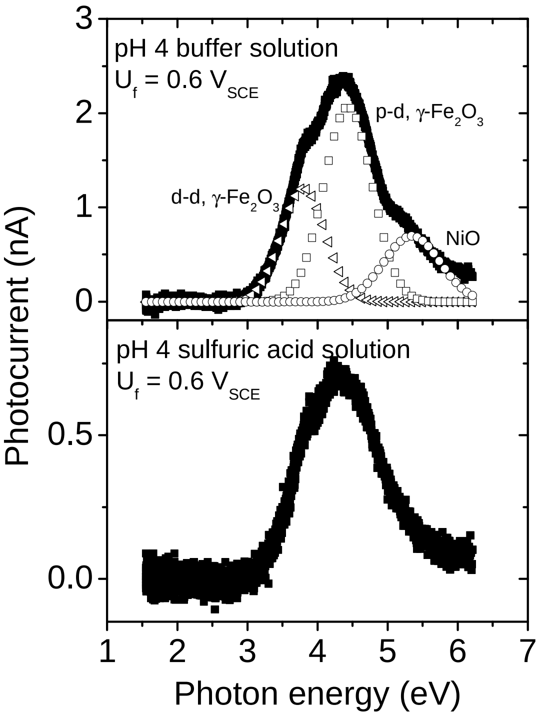

Fig. 1 Photocurrent spectra of the passive film formed on Fe-20Cr-15Ni in pH 4.0 (a) borate buffer solution and (b) sulfuric acid solution.