Variation in the Surface Charge of Stainless Steel by Surface Treatment : Role of Surface Hydroxyl Groups

Satoshi FUKUZAKI*, Hiromi URANO*, and Minoru HIRAMATSU*

表面処理によるステンレス鋼の表面電荷の変動：表面水酸基の役割

福崎 智司*, 浦野 博水*, 平松 実*

Key Words : Stainless steel, Surface Charge, Hydroxyl Group, Potentiometric Titration, Water Vapor Adsorption

Introduction

Passive film on stainless steel consists mainly of chromium oxide and hydroxide^{1), 2)}. In general, the surfaces of solid oxide and hydroxide are covered by hydroxyl groups formed by hydration of the virgin surface^{3), 4)}. Since the surface charge of stainless steel is established by amphoteric dissociation of hydroxyl groups, the density and property of hydroxyl groups govern the electrostatic nature. The relative sign and magnitude of the surface charge of stainless steel have an influence on the surface reactivity such as adsorption of electrolytic contaminants in aqueous solution. Although the composition of passive film on stainless steel is known to depend on the conditions of passivation and pretreatment^{1), 2)}, little is known about the variation in the electrostatic nature of stainless steel surface by various pretreatments.

In this study, the effect of pretreatment with heat or solutions of different pH on the surface charge of stainless steel was studied, using non-porous stainless steel particles, by a surface titration methodology.

Experimental

Materials.—Nonporous stainless steel particles (SUS 316L) were obtained from Yasui Kikai Co., Ltd. (Osaka). The specific surface area, determined by the N₂ adsorption method, of stainless steel particles was 0.4m²/g. Before use, stainless steel particles were washed with acetone and ethanol, and dried at 100°C.

Pretreatment.—The 20-g aliquot of stainless steel particles was (i) heated in a furnace under an atmosphere at the temperature range of 100 to 500°C for 4h, or (ii) immersed in 200ml of pre-

Fig. 1 Adsorption isotherms of water vapor onto heat-treated stainless steel particles at 25°C.

treatment solutions of different pH, which was adjusted over a pH range of 2 to 9 with HNO₃ and KOH, for 2h followed by rinsed with deionized water, and then dried at 100°C.

Water vapor adsorption.—Water vapor adsorption was conducted at 25°C using an automatic adsorption apparatus (Belsorp 18; Bel Japan inc., Osaka) equipped with a data-processing computer. In monolayer range, the adsorption isotherm was analyzed using the linear BET equation and a linear regression method:

$$P/V(P_0 - P) = 1/V_m c + [(c-1)/V_m c](P/P_0) \quad \dots\dots\dots(1)$$

where V is the amount of water vapor adsorbed, mL/m²; V_m is the maximum value of V in monolayer; P and P_0 are the equilibrium and saturated vapor pressure, respectively, Torr; and c is a constant.

Potentiometric titration.—The surface charge density (σ) of stainless steel particles was measured in 10⁻³M KNO₃ solution in a pH range of 3.4 to 10, using a potentiometric titrator (GT-07, Mitsubishi Chemical Ind. Ltd., Tokyo) as described previously⁵⁾.

*Ind. Technol. Center. of Okayama (5301 Haga, Okayama-shi, Okayama 701-1296, Japan)
岡山県工業技術センター

Fig. 2 The σ profiles of heat-treated stainless steel particles as a function of pH.

Results and Discussion

Figure 1 shows the isotherms for water vapor adsorption on stainless steel particles after heat treatment. BET-type isotherms with different initial slopes were obtained, and therefore Eq. 1 was fitted to the adsorption data. With increasing temperature from 100 to 500°C, the BET c constant, reflecting the adsorption affinity of water vapor, and V_m decreased from 26.0 to 18.5 and from 0.31 to 0.19 mL/m², respectively. Clearly, lower c and V_m values imply the decrease in the number of adsorptive sites on stainless steel surfaces for water vapor. In general, a dehydroxylated oxide surface is known to be characterized by a lower affinity for water than a hydroxylated surface⁶⁾. The results indicated that the density of hydroxyl groups on stainless steel surfaces decreased through their removal by heat treatment.

Figure 2 shows the σ profiles of the heat-treated stainless steel particles as a function of pH. Large differences were observed in the positive σ region. With increasing temperature, the positive σ value decreased markedly and the isoelectric point (IEP) shifted gradually from pH 8.9 (100°C) to 6.4 (500°C). Similar shift of the IEP to the acidic side has been reported for the heat treatment of α -alumina particles having fully hydrated surface⁷⁾. It is likely that the change in the IEP was due to the degree of hydroxylation of stainless steel surfaces.

Figure 3 shows the variation in the σ profiles of stainless steel particles after treatment with solutions of different pH. With decreasing solution pH from 9 to 2, the σ value of the stainless steel decreased, especially in the positive region, accompanied by a shift of the IEP from pH 7.8 to 6.8. In order to clarify the relationship between

Fig. 3 The σ profiles of stainless steel particles treated with solutions of different pH, as a function of pH.

the σ and surface hydroxyl groups, the water vapor isotherms were also measured. The isotherms showed small but significant changes in the initial slopes, which became gentler with decreasing solution pH, *i.e.*, lower affinity characters (data not shown). The BET c constant, derived by a data-fitting procedure using Eq. 1, decreased gradually from 30.6 (pH 9) to 21.4 (pH 2), with slight variations in V_m (0.31 to 0.29 mL/m²). These results suggested that the surfaces having the lower densities of hydroxyl groups were formed by the treatment with solutions of lower pH.

Conclusion

The variation in the surface charge of stainless steel was successfully assessed by a potentiometric titration method. As a result of pretreatment with heat or solutions of different pH, the electrostatic nature of stainless steel surface changed markedly. The shifts of the σ profile and the IEP to the acidic side were interpreted as arising from the decrease in the density of hydroxyl groups on the stainless steel surface.

(Received April 10, 1998; Accepted June 10, 1998)

References

- 1) B. Elsener and A. Rossi; *Mater. Sci. Forum*, **192-194**, 225 (1995)
- 2) K. Asami and K. Hashimoto; *Corros. Sci.*, **19**, 1007 (1979)
- 3) G. A. Parks; *Chem. Rev.*, **65**, 177 (1965)
- 4) G. A. Parks and P. L. de Bruyn; *J. Phys. Chem.*, **66**, 967 (1962)
- 5) S. Fukuzaki, H. Urano, and K. Nagata; *J. Ferment. Bioeng.*, **81**, 163 (1996)
- 6) A. C. Zettlemoyer; *J. Colloid Interface Sci.*, **28**, 343 (1968)
- 7) M. Robinson, J. A. Pask, and D. W. Fuerstenau; *J. Am. Ceram. Soc.*, **47**, 516 (1964)