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Vibrating Phenomenon for Electrode Reaction of Mild Steel in Aqueous Ethanol Solution Containing Sulfuric Acid

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It was found that natural electrode potential (NEP) of mild steel electrode vibrates in aqueous ethanol solution containing sulfuric acid. By in situ analysis of electrochemical impedance spectroscopy, this vibrating phenomenon is based on the transition between passivation (passive region) and active dissolution (active region) of the mild steel electrode.

It has been reported by some workers that electric signals vibrate for various electrode reactions in solution systems.1-5) However, it is difficult to analyze the vibrating phenomena as the system was under either complicating or severe corrosive conditions. In this communication, it was found that the vibrating phenomenon of natural electrode potential (NEP) took place in the electrode reaction system of mild steel immersed in 90% aqueous ethanol solution containing small amount of sulfuric acid (H_2SO_4). The mechanism was analyzed *in situ* by measurement of electrochemical impedance spectroscopy (EIS).

The plates (20 x 20 x 1.35 mm^3) and the disks (2.0 mmϕ) of mild steel (JIS SS 41) were polished with emery papers up to 1500 grade. They were subsequently defatted in methanol (reagent grade) and washed ultrasonically (bath-type, 125 W) in acetone (reagent grade) to use as the working electrode. Counter and reference electrodes were the platinum sheet (30 x 40 x 0.5 mm^3) and the saturated calomel electrode (SCE), respectively. The testing solution was aqueous 90vol% ethanol solution containing H_2SO_4 (0.1 - 1.0 M). Ethanol and water were distilled once and three times, respectively.

All electrochemical measurements were carried out after the working electrode was cathodically polarized at -1.2 V *vs.* SCE for 10 min. The NEP of mild steel in the ethanol solution was measured by the electrometer (Hokuto Denko, HE-106) for 1 day. The polarization measurement was immediately conducted by the potentiodynamic method with a scanning rate of 50 mV/min (Hokuto Denko, Potentiostat/Galvanostat HA-501, Function generator HB-104). The EIS measurement was carried out by a frequency response analyzer (FRA; NF Electronic Instruments, FRA-5020), potentiostat (Toho Technical Research, P/G-2000) and a data processor (personal computer, NEC, PC-9800) in the frequency range of 20 kHz to 10 mHz. The reference signal voltage of sinusoidal wave was 3.5 mV (RMS).

NEP vs. immersion time curves of SS 41 were measured in 90% aqueous ethanol solutions containing various contents of H_2SO_4 at room temperature (Fig. 1). In 90% ethanol solution containing 0.5 M or 1.0 M H_2SO_4, the NEP of SS 41 was not changed and kept constant after immersion for 10 h (Fig. 1(i)-(ii)). But, the NEP in 90% ethanol-0.1 M H_2SO_4 solution vibrated regularly (self-passivation time (T_a) = 10.2 h,$^{6)}$ amplitude = 0.18 V, cyclic period = 3.5 min, Fig. 1(iii)).

The cathodic and anodic polarization curves of SS 41 steel in 90% ethanol-0.1 M H_2SO_4 solution at room temperature where vibrating phenomenon occurred were shown in Fig. 2. A, B, and C in this figure represent the point at minimum NEP value for the potential vibration (-0.5 V vs. SCE), the point at NEP value between A and C (-0.35 V vs. SCE) and the point at maximum NEP value for potential vibration (-0.30 vs. SCE), respectively. According to this figure, A and C point are near the corrosion potential and the active dissolution peak, respectively. The corrosion reactions at A and C points might be correspond to the stage of active dissolution and the pre-stage or initial stage of passivation, respectively. It is reported that the vibrating phenomena of NEP take

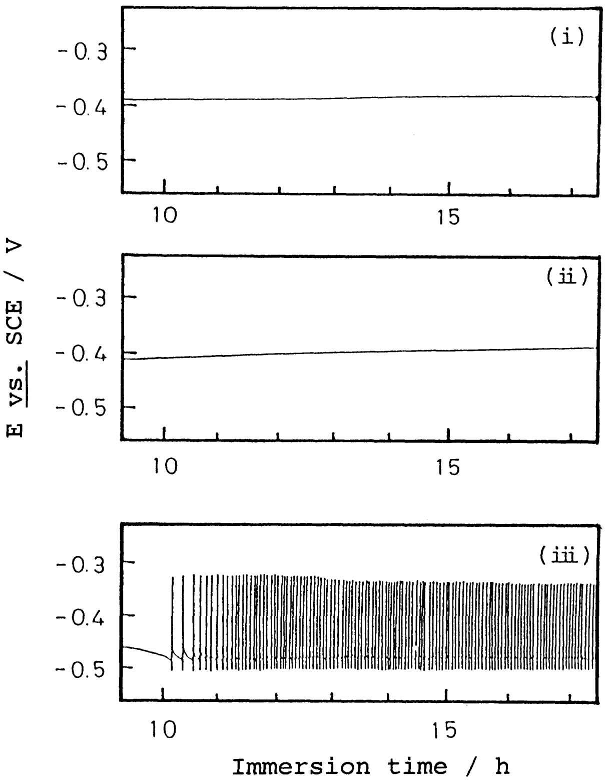

Fig. 1. Natural electrode potential vs. immersion time curves of SS 41 steel in 90% ethanol solution containing H_2SO_4 at room temperature.
(i) 1.0 M H_2SO_4, (ii) 0.5 M H_2SO_4, and (iii) 0.1 M H_2SO_4.

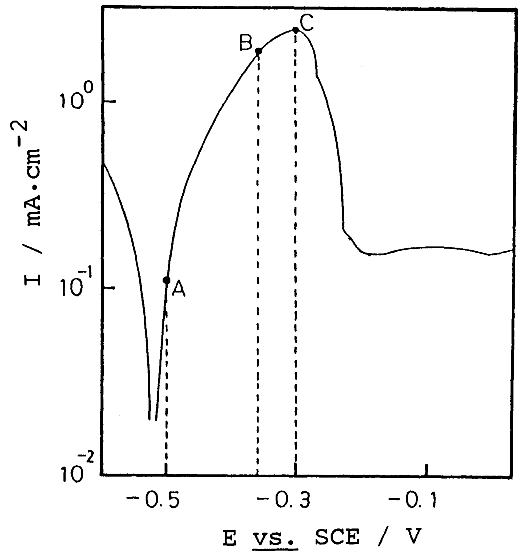

Fig. 2. Polarization curve of SS 41 steel in 90% ethanol-0.1 M H_2SO_4 solution at room temperature.
A; point at minimum NEP value (-0.50 V vs. SCE), B; point between A and C points (-0.35 V vs. SCE), and C; point at maximum NEP value (-0.30 V vs. SCE).

place for some stainless steels in conc. H_2SO_4 solution at high temperature, and are based on reversible transition between active and passive regions, i.e. the repetition of formation and destruction of passivated film by polarization curve measurement.[6b,7] Similarly, the regular oscillations of current, which appeared at the potentiostatical study for iron electrode in aqueous H_2SO_4 solutions, are based on the repetition of the dissolution and the formation of passive film of iron.[2,8] However, in this case, the vibrating phenomenon could not be obviously evaluated by polarization curve measurement, which is a static measurement.

To evaluate by the dynamic and *in situ* method, the vibrating phenomenon of NEP was measured by the electrochemical impedance spectroscopy (EIS). The Cole-Cole plots were shown in Fig. 3. At A point, Cole-Cole plot showed a capacitive arc in high frequency and an inductive arc in low frequency range. The former arc is based on the relaxation of capacitance (C_{dl}) in electric double-layer and charge transfer resistance (R_{ct}) (C_{dl} = 2.3 x 10^{-5} F/cm^2, R_{ct} = 5.0 x 10^3 Ω). The latter arc might be attributable to the adsorption intermediate in dissolution reaction of iron under low anodic polarization.[9] At C point, the Cole-Cole plot showed two capacitive arcs based on electric double-layer (arc in high frequency) and on passive film (arc in low frequency). The Cole-Cole plot at B point which is between A and C showed two and more capacitive arcs. The arc in high frequency is due to capacitance in electric double-layer. The capacitance arc with negative resistance in low frequency is thought to be based on passive reaction.[9b,10] The vibrating phenomenon of the NEP that was shown in Fig. 1(iii) occurred by dynamic transition between passivation (passive region) and active dissolution (active region) of the mild steel electrode.

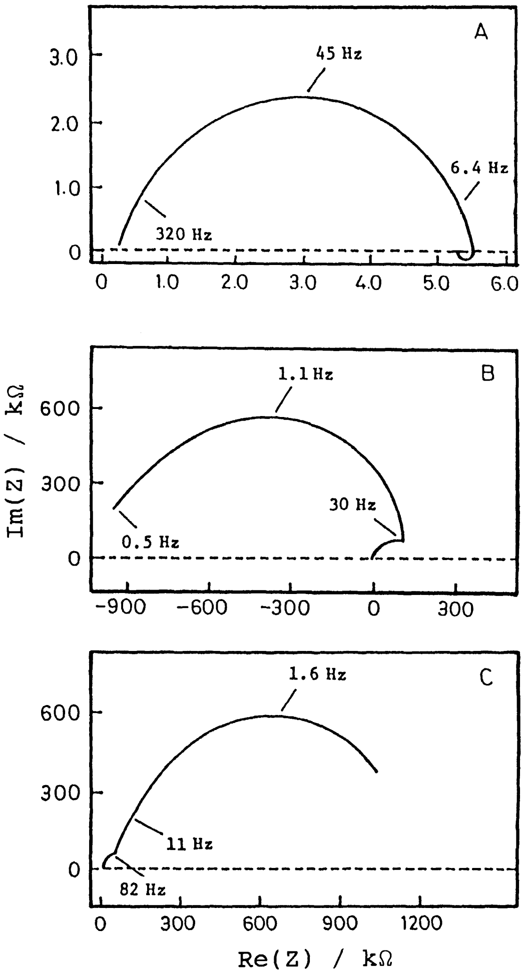

Fig. 3. Cole-Cole plots of SS 41 steel in 90% ethanol-0.1 M H_2SO_4 solution at room temperature. A, B and C correspond to A, B and C points as shown in Fig. 2.

Anyhow, it was found that the NEP of mild steel electrode vibrated in aqueous ethanol solution containing sulfuric acid. This vibrating phenomenon is analyzed by in situ analysis of electrochemical impedance spectroscopy. Further details of the mechanism will be studied in future.

References

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