Mechanism of Corrosion Inhibition with Bismuth Compounds for Iron, Nickel and Zinc in Acid Solutions

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Formation of a highly corrosion-protective and persistent film on iron with bismuth (III) chloride in acid solutions has been reported in our previous paper. In order to investigate the inhibition mechanism of metallic corrosion with bismuth (III) compounds in acid solutions, inhibition efficiencies of the compounds for iron, nickel, and zinc in 1N HClO₄ were determined by polarization measurements. X-ray photoelectron spectra showed that the protective films formed on the metal were composed of an outer layer comprising metallic (Fe²⁺, Ni²⁺ or Zn²⁺) and Bi³⁺ oxides and an inner layer consisting of metallic bismuth. Dramatic inhibition effects of the inhibitors are attributed to the coating of metallic bismuth with a high hydrogen-overpotential on the almost whole area of metal substrate and to the adsorption of an inhibitive anion on the faintly exposed area of metal substrate covered with the outer layer.

1 INTRODUCTION

A series of investigations¹⁻⁴⁾ have dealt with inhibition effects of inhibitors including typical elements of high atomic numbers on metallic corrosion. A new type of corrosion inhibitors, organo-antimony¹⁻³⁾ and organobismuth⁴⁾ compounds have been examined for iron and nickel in acid solutions. They form highly persistent and protective films on the iron surface in acid solutions, resulting in high inhibition efficiencies even at low concentrations. The films thus formed on the iron surface consist of multiple layers: an outer layer composed of Fe(II) and Sb(III) or Bi(III) oxides and an inner

layer of metallic antimony or bismuth.

The inhibition efficiency of Bi(III) chloride has been measured for iron corrosion in 1N HClO₄, 1N HCl, and 1N H₂SO₄⁵⁾. This compound is an excellent inhibitor by forming a protective film against iron corrosion. The film, comprising an outer layer composed of oxides and an inner one of metallic bismuth, is remarkably persistent against corrosion in an acid solution without the inhibitor. The high inhibition efficiency is mainly attributed to the outer and inner layer and the marked persistence to the inner layer. Bismuth (III) chloride surpasses organoantimony and organobismuth compounds in stability against oxidation with oxygen and are less toxic by far than antimony compounds.

This work was undertaken to investigate the mechanism of corrosion inhibition for iron, nickel, and zinc in an acid solution with bismuth(III) compounds by polarization measurements and cyclic voltammetry. The

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protective films formed on the metals with the bismuth compounds were analyzed by X-ray photoelectron spectroscopy (XPS) and electron-probe microanalysis (EPMA).

2 EXPERIMENTAL

Inhibitors used in this study were bismuth(III) chloride, iodide, sulfate, and oxide. An acid solution, 1N HClO₄ was prepared by diluting an analytical reagent with redistilled water and deaerated by passing a nitrogen gas through it.

Disks of 99.9% Fe, 99.99% Ni, and 99.99% Zn (10.0 mm diam) were fixed at the end of a glass tube holder with a thermo-shrinkable Teflon tube and epoxy adhesive. A rod of 99.9999% Bi (8.0 mm diam) was embedded in a Teflon holder. The surface of these metallic electrodes was prepared in the same manner as has been described¹⁾. The electrodes except the bismuth one were discarded following each run of measurements because a layer of bismuth deposit could not be removed completely from the electrode surface by abrasion with emery papers.

Polarization curves of iron, nickel, zinc and bismuth electrodes were potentiostatically measured in deaerated 1N HClO₄ with and without the inhibitor at 30°C. The potential was referred to a saturated calomel electrode(SCE). Cyclic voltammetry for the bismuth electrode was carried out in 1N HClO₄ containing 1×10⁻⁴M (mol dm⁻³) of BiCl₃ at the scan rate of 0.1 V s⁻¹ under a nitrogen atmosphere.

X-ray photoelectron spectra of the protective films formed on the nickel and zinc surfaces were measured using JEOL-90SX spectrometer with Mg K_α radiation as an X-ray source. The nickel and zinc disks were previously treated with bismuth chloride at 1×10⁻⁴M in a deaerated 1N HClO₄ solution at 30°C for 1 h. The treated disks were rinsed with water, dried under vacuum overnight, mounted on a standard sample probe and placed in a sample chamber of the spectrometer. All

manipulations after prior treatment were carried out under a nitrogen atmosphere.

The binding energies for components of interests, Ni(2p), Zn(2p), O(1s), Cl(2p), and Bi(4f) were referred to the binding energy of C (1s_{1/2}) at 284.6 eV. In order to observe depth profiles of components in the protective films, an ion bombardment of the films was carried out with an Ar⁺ gun. The sputtering time of 1 min corresponds to about 50 nm in depth.

The iron disks treated with bismuth chloride and sulfate at 1×10⁻⁴M in deaerated 1N HClO₄ at 30°C for 1 h were rinsed with water under a nitrogen atmosphere and dried under vacuum overnight. Line analyses of elements, Fe, Bi, Cl, and S at the surfaces of the iron disks were performed using a Shimadzu EPMA-8703 analyzer after a SEM image observation.

3 RESULTS AND DISCUSSION

3.1 Inhibition effects of BiCl₃ on corrosion of iron, nickel and zinc in 1N HClO₄.

Fig. 1 Polarization curves (potential E and current density i) of nickel in 1N HClO₄ without (—) and with BiCl₃ at 1×10⁻⁶M (---), 1×10⁻⁵M (— · —), and 1×10⁻⁴M (----).

Polarization curves of the nickel and zinc electrode in 1N HClO₄ with and without BiCl₃ at various concentrations are shown in Figs. 1 and 2, respectively. Bismuth chloride suppressed both the anodic and cathodic reactions of nickel and zinc corrosion as well as iron corrosion.

The corrosion potential E_{cor} and the corrosion current density were obtained by extrapolating the anodic and cathodic Tafel lines. The values of E_{cor} for the nickel and zinc electrodes inhibited with BiCl₃ at concentrations between 1×10^{-8} and 1×10^{-4} M shifted toward a noble potential at most by 30 mV from the value of the uninhibited electrode. Only an exception was E_{cor} of the nickel electrode inhibited with 1×10^{-4} M of BiCl₃, shifting by 120 mV from the value of the uninhibited one.

The inhibition efficiency I was obtained by

$$I / \% = 100(1 - i_{cor}/i_{cor}^0) \quad (1)$$

where i_{cor} and i_{cor}^0 represent the corrosion current densities of the inhibited

Fig. 2 Polarization curves of zinc in 1N HClO₄ without (—) and with BiCl₃ at 1×10^{-9} M (---), 1×10^{-7} M (— · —), 1×10^{-6} M (---), and 1×10^{-4} M (— · —).

Fig. 3 Inhibition efficiency I of BiCl₃ at various concentrations c in 1N HClO₄ for iron (○), nickel (□), and zinc (△).

and uninhibited electrode, respectively. Figure 3 shows inhibition efficiencies of BiCl₃ for nickel and zinc in 1N HClO₄, together with the values for the iron electrode previously reported⁵⁾. Bismuth chloride was an efficient inhibitor for zinc, of which I values (more than 98% at 1×10^{-6} M) are comparable with those for iron. This inhibitor was, however, less effective on nickel corrosion in 1N HClO₄, indicating about 70% of I at 1×10^{-4} M.

3.2 Structures of protective films on iron, nickel, and zinc electrodes.

X-ray photoelectron spectra of components, (a) nickel, (b) oxygen, (c) chlorine, and (d) bismuth for the protective film formed on the nickel electrode and their depth profiles are shown in Fig. 4. At the outermost part of the film (sputtering time $t_s = 0$ s), peaks of Ni(2p_{3/2}), O(1s_{1/2}), and Bi(4f_{7/2}) appeared at 856.5, 532.5, and 156.6 eV of the binding energy, indicating the presence of Ni²⁺, O²⁻ combined with H⁺, and Bi³⁺, respectively. Intensities of the Ni²⁺ and Bi³⁺ peak increased and then decreased with an increase in t_s . A peak of zero-valent nickel appeared at 852.5 eV inside the film and the intensity increased with t_s . A peak of O(1s_{1/2}) emerged at 530.1 eV, being indicative of the presence of O²⁻ in the film. Chlo-

Fig. 4 Depth profiles in XPS of Ni(2p_{3/2}) (a), O(1s_{1/2}) (b), Cl(2p) (c), and Bi(4f_{7/2}) (d) for the nickel electrode pre-treated with 1×10⁻⁴M of BiCl₃ in 1N HClO₄ for 1 h at the sputtering time t_s.

Fig. 5 Depth profiles in XPS of Zn(2p_{3/2}) (a), O(1s_{1/2}) (b), Cl(2p) (c), and Bi(4f_{7/2}) (d) for the zinc electrode pre-treated with 1×10⁻⁴M of BiCl₃ in 1N HClO₄ for 1 h at the sputtering time t_s.

ride ion was also present in the film since there was a peak of Cl(2p) at 198.7 eV in the range of t_s between 0 and 30 s. A peak of Bi(4f_{7/2}) appeared at 156.6 eV, showing the presence of atomic bismuth at the surface and inside of the film.

These spectral observations result in a structural image of the protective film at the nickel surface; the film consists of

two layers, an outer layer composed of Ni²⁺, Bi³⁺, O²⁻, and Cl⁻ and an inner layer of metallic bismuth. This structure resembles that of the film formed on iron with BiCl₃ except for higher contents of Cl⁻ and Bi³⁺ inside the film on nickel than iron.

Figure 5 shows X-ray photoelectron spectra of the protective film formed on zinc in 1N HClO₄ with BiCl₃ for 1 h. A peak of Zn(2p_{3/2}) appeared at 1022.7 eV, indicating the presence of Zn²⁺ at the outermost of the film. The binding energy of the peak shifted to 1021.4 eV with an increase in the sputtering time, implying a gradual change of components from Zn²⁺ to metallic zinc with the depth from the surface. The film seemed to be thinner and the content of metallic bismuth higher than the film formed on nickel. There was Bi³⁺ only at the surface of the film. Thus, the film on zinc consists of an outer layer composed of Zn²⁺ and O²⁻ and an inner layer of metallic bismuth. Protective films formed on the iron, nickel, and zinc surfaces in 1N HClO₄ with BiCl₃ are schematically illustrated in Fig. 6.

3.3 Formation of protective films on metal surfaces.

Leidheiser, Jr.⁶⁾ has suggested a possibility of corrosion inhibition by metallic cations including Bi³⁺ with the formation of a reduced bismuth layer on the surface of a corroding metal. If the protective film is formed by combination of a cathodic bismuth deposition,

and anodic dissolution of a substrate metal M,

the facility of these processes should depend on the difference in the equilibrium potential between bismuth and substrate metals. Since the standard electrode potential of bismuth is 0.317 V vs. NHE⁷⁾, the facility of reactions on metals is in the order, nickel < iron <

Fig. 6 Structures of the protective films formed on iron (a), nickel (b), and zinc (c) with BiCl_3 in 1N HClO_4 .

zinc. The higher concentration of Bi^{3+} in the outer layer of the film on nickel than on iron and zinc may imply incompleteness of the film formation on nickel treated with BiCl_3 for 1 h. Contrarily, the absence of Bi^{3+} in the outer layer on zinc is attributed to the complete deposition of bismuth caused by a large electromotive force between zinc and bismuth electrodes.

3.4 Inhibition mechanism of the protective film against metal corrosion.

It has been reported in the previous paper⁵⁾ that the corrosion potential of an iron electrode inhibited with BiCl_3 in acid solutions shifted scarcely from the potential of an uninhibited electrode. Polarization curves shown in Figs. 1 and 2 exhibit little changes of the corrosion potential from the value of uninhibited electrode with an exception of the case for nickel at $1 \times 10^{-4}\text{M}$ of BiCl_3 . These results suggest that corrosion processes occurring on the metal surface covered with the protective film are cathodic hydrogen evolution reaction and anodic metal dissolution.

As shown in Fig. 6, most of the surface area of the substrate metal is overlaid with the inner layer of metallic bismuth. In order to clarify the corrosion proc-

esses on a coupled electrode with a small area of iron to a large area of bismuth in an acid solution, the corrosion potential of the coupled electrode at which the ratio of areas for iron to bismuth is 1 to 500 was measured in 1N HClO_4 . The potential of this electrode, -0.485 V vs. SCE was nearly equal to the potential of an iron electrode in 1N HClO_4 , -0.490 V , indicating no change of the corrosion process on the iron substrate coated with large area of metallic bismuth. The positive shift of the corrosion potential for nickel electrode in the presence of BiCl_3 at $1 \times 10^{-4}\text{M}$ may be attributed to the formation of a passive film on the surface of substrate nickel.

Taking the structures of the protective films on metals into consideration, it seems reasonable that the metal dissolution reaction occurs on the surface of substrate metal uncovered with the inner bismuth layer but covered with the outer oxide layer. However, it remains ambiguous whether the hydrogen evolution reaction occurs on the surface of bismuth layer or on the uncovered area of substrate surface. Figure 7 shows polarization curves of bismuth and iron electrodes in 1N HClO_4 with BiCl_3 at $1 \times 10^{-4}\text{M}$. The cathodic current density for the bismuth electrode was remarkably low and constant in the potential region between -0.2 and -0.65 V . This indicates that bismuth is

Fig. 7 Polarization curves of bismuth (—) and iron electrodes in 1N HClO_4 with BiCl_3 (---) and BiI_3 (— · —) at $1 \times 10^{-4}\text{M}$.

Fig. 8 Cyclic voltammogram for bismuth electrode in 1N HClO_4 containing $1 \times 10^{-4}\text{M}$ BiCl_3 at the sweep rate of 0.1 Vs^{-1} .

classified as one of high overpotential metals. Since the current density was markedly low in the potential range corresponding to the Tafel region in the cathodic polarization curve for the iron electrode, the hydrogen evolution reaction must occur at a small area of the surface uncovered with the bismuth metal layer. A cyclic voltammogram for the bismuth electrode in 1N HClO_4 containing $1 \times 10^{-4}\text{M}$ of BiCl_3 showed a drastic increase of the cathodic current for the hydrogen evolution reaction at a more negative potential than about -1.1 V , as shown in Fig. 8. It is, thus, presumed that the hydrogen evolution reaction can hardly be inhibited by the formation of bismuth layer on the surface of a metal whose corrosion potential in an acid solution is more negative than -1.1 V .

Since the cathodic current density of the bismuth electrode (Fig. 7) was not markedly lower as compared with that of the uninhibited nickel at the potential in the Tafel region (Fig. 1), BiCl_3 in 1N HClO_4 cannot suppress the cathodic reaction on nickel to more extents than on iron and zinc, resulting in the lower inhibition efficiency for nickel as shown in Fig. 3. It is thus concluded that the inhibition of the cathodic reaction on the iron, nickel, and zinc electrode covered with the protective film is ascribed to the high hydrogen overpotential of metal-

Fig. 9 Inhibition efficiency I of BiI_3 ($\circ$), BiCl_3 (Δ), $\text{Bi}_2(\text{SO}_4)_3$ ($\square$), and Bi_2O_3 (∇) for iron in 1N HClO_4 .

lic bismuth deposited on the substrate surface.

Provided that both the anodic and cathodic processes of corrosion reaction occur at the substrate metal surface uncovered with the inner bismuth layer, the corrosion current density can partly be associated with adsorption of an anion on the substrate surface. The specifically adsorbed anion on the iron surface inhibits or stimulates the anodic process of iron corrosion in an acid solution⁸⁾. Since the adsorbability of anions on the iron surface in 1N HClO_4 is closely related to the hard and soft acids and bases principle (HSAB principle)⁹⁾, inhibition effects of anions on iron corrosion in 1N HClO_4 decrease in the order^{10, 11)}, according to the order of softnesses as bases,

The inhibition efficiencies of BiI_3 , BiCl_3 , $\text{Bi}_2(\text{SO}_4)_3$, and Bi_2O_3 were obtained for iron in 1N HClO_4 at various concentrations by polarization measurements and are shown in Fig. 9. The order of the inhibition efficiencies was as follows:

Fig. 10 SEM photographs of the protective film formed on iron with prior treatment of BiCl_3 in 1N HClO_4 (a and c) and X-ray intensities of Fe, Bi, and Cl with linear scans from A to B (b and d).

The adsorbed anion on iron is considered to be ClO_4^- in a 1N HClO_4 solution of Bi_2O_3 . The order of inhibition efficiencies for bismuth compounds agreed with the order of adsorption abilities for inhibitive anions, indicating that the adsorption of anion is closely associated with the inhibition of iron corrosion.

Because this order of anions is basically inapplicable to their adsorption on an oxide but a bulk metal¹²⁻¹³⁾, the inhibition can be attributed to the adsorption on the surface of the iron substrate. In order to investigate the adsorption of anion at an uncovered area of the iron substrate, an electron-probe microanalysis of the iron surface pre-treated with BiCl_3 or $\text{Bi}_2(\text{SO}_4)_3$ in 1N HClO_4 for 1 h was carried out after SEM observation.

Figure 10 shows SEM photographs (a and c) and line analysis of components, Fe, Bi, and Cl with linear scans from A to B

in (a) and (c) (b and d) for the protective film afforded by BiCl_3 in 1N HClO_4 . Photograph (a) shows a uniform appearance of the protective film surface. An X-ray spectrum of line analysis exhibits constant X-ray intensities of elements, Fe and Bi on the whole area of electrode surface, indicating uniform distribution of elements on the surface. A small spot, which had not been observed in the previous study⁵⁾, was rarely found on the surface, as shown in (c). X-ray intensities of Fe, Bi, and Cl with a scan through the spot from A to B in (c) showed a decrease in the content of Bi and an increase in that of Cl at the spot, implying an area of the iron surface uncovered with bismuth and adsorption of Cl^- . On the other hand, the intensity of Cl is almost zero at the area where the intensity of Bi is high and constant. It is concluded from these results that Cl^- is

not specifically adsorbed on a large area of the deposited bismuth but on a small area of the substrate iron. A SEM photograph of the iron surface pre-treated with $\text{Bi}_2(\text{SO}_4)_3$ also showed the presence of an area uncovered with bismuth and the X-ray intensity of S implied a slight amount of adsorbed sulfate ion at the area, resulting in the lower inhibition efficiency of sulfate than chloride.

Polarization curves of the iron electrode in 1N HClO_4 with BiI_3 at $1 \times 10^{-4} \text{M}$ are shown in Fig. 7, indicating that BiI_3 suppresses the anodic reaction to a more extent than BiCl_3 . Consequently, a remarkably high value, 99.7% of the inhibition efficiency was obtained for iron in 1N HClO_4 with BiI_3 at $1 \times 10^{-4} \text{M}$.

4 CONCLUSION

Bismuth (III) chloride is an excellent corrosion inhibitor for iron and zinc in 1N HClO_4 but that is not the case for nickel. The inhibitor forms a protective film on the surface of a substrate metal; The film consists of two layers, an outer layer comprising Bi^{3+} and metallic oxide and an inner layer composed of metallic bismuth, except for lacking in inclusion of Bi^{3+} inside the outer layer on zinc. Corrosion processes of the substrate metal covered with the protective film in acid solutions are the cathodic hydrogen evolution and the anodic metal dissolution reactions on the metal uncovered with the bismuth layer. The inhibition effect of the protective film on metal corrosion is mainly attributed to the coverage of the surface with the bismuth layer of which the hydrogen overpotential is high, to the

coverage with the oxide layer and to the anion adsorption on the substrate metal.

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