Technical Report

UDC 546 . 47 . 13 - 381 : 620 . 193 . 2

Ion Permselectivity of Artificially Synthesized Zinc Corrosion Product Films

Mamoru SAITO* Kohei TOKUDA
Nobuyuki SHIMODA

Abstract

Zinc hydroxychloride ($Zn_5(OH)_8Cl_2 \cdot H_2O$) is well-known as a typical corrosion product of zinc coated steel sheets. We evaluated zinc hydroxychloride's transport number of chloride ion to study barrier effects on permeation of corrosion factor. Zinc hydroxychloride was formed into the semipermeable membrane with precipitation reaction between zinc ion and hydroxide ion. We measured its membrane potential in 0.001 M ~ 1 M potassium chloride solution. As the result of membrane potential measurement, we found that the ion permselectivity of the film was anionic. And its transport number of chloride ion was 0.58, smaller than that of iron (III) oxide (0.96). Since, it is possible that zinc hydroxychloride's barrier effect on permeation of corrosion factor is high.

1. Introduction

With the aim of preventing the corrosion of steel materials susceptible to corrosion, the zinc-coated steel sheet is widely used in automobile bodies, home appliances, and buildings.

Figure 1 shows the typical mechanism of corrosion of zinc-coated steel sheets.[1] The zinc-coated steel sheet is equipped with three types of corrosion preventive functions as follows: (1) the zinc coat serving as a barrier to corrosion factor, (2) the sacrificial corrosion of the zinc making contact with the base metal, and (3) corrosion products of zinc helping to restrain the base metal corrosion.[2]

In the case of Zn-11%Al-3%Mg-0.2%Si alloy-coated steel sheet, which is added with alloying elements other than Zn, it is said that the corrosion resistance improves because zinc hydroxychloride [$Zn_5(OH)_8Cl_2H_2O$], which apparently serves as a barrier to the permeation of corrosion factors, is not decomposed into zinc oxide (ZnO) and is stabilized.[3] However, it has not yet been clarified which of the properties of zinc hydroxychloride (ion permselectivity, electrical resistance, and density) contributes to the barrier effect the most. For example, by examining the ion permselectivity of zinc hydroxychloride, it is possible to evaluate the transport number of Cl^-, which influences corrosion significantly. In the past, the ion permselectivity of corrosion product of iron was evaluated. As a result, it was found that the transport number of Cl^- was large, whereas the barrier effect of corrosion product was small.[4, 5] It is considered that when the corrosion product's transport number of Cl^- is large, the corrosion of base metal is promoted, since more and more Cl- reach the base metal.[4, 5] The transport number of Cl^- can be evaluated by measuring the membrane potential.

If there is a difference in anion's and cation's concentration around both sides of a film, membrane potential occurs there. Absolute value of membrane potential decides the extent of ion permselectivity. If the value of the membrane potential is positive, anions can pass through a film easily, whereas if it is negative, cations can pass through it. In

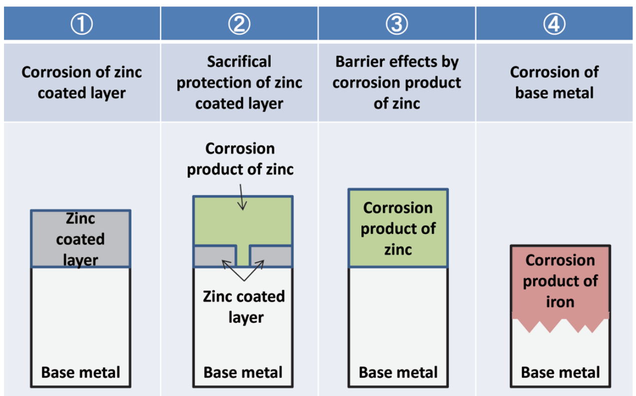

Fig. 1 Corrosion model of zinc coated steel sheets

* Surface Treatment Research Lab., Steel Research Laboratories
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

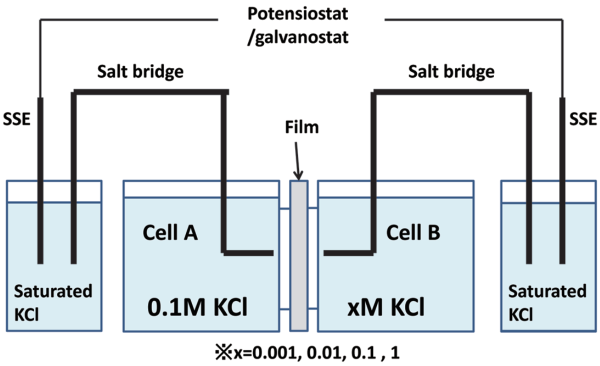

Fig. 2 Schematic diagram of membrane potential measurement

general, we can determine the ion's transport number from the value of membrane potential. **Figure 2** schematically shows the equipment for measuring the membrane potential. Membrane potential is expressed as follows.[4)]

$$\Delta\varphi = \varphi_B - \varphi_A = (t^+ - t^-)(RT/F) \ln (C_B/C_A) \qquad (1)$$

where, $\Delta\varphi$ denotes membrane potential; φ_A/φ_B, potential in cell A/B; t^+, transport number of cations; t^-, transport number of anions ($t^+ + t^- = 1$); R, gas constant; T, temperature; F, Faraday constant; and C_A/C_B, electrolyte concentration of aqueous solution in cell A/B.

2. Experimental Procedure

2.1 Preparation of samples

The film like zinc hydroxychloride is essential for measurement of membrane potential. We selected the chemical precipitation process to prepare the film of zinc hydroxychloride. **Figure 3** shows a chemical compound film-making equipment. Cellophane semipermeable membrane (M-5, KENIS Ltd.) was inserted between cell (i) and cell (ii). The cell (i) was filled with 0.5M $ZnCl_2$, and cell (ii) with 0.1M NaOH. This condition was retained at room temperature for 72 hours. Thereafter the chemical compounds were formed into the semipermeable membrane. The compound film was labeled as ZC-1. After that, the solutions in both cells were replaced with 2M $ZnCl_2$, and retained at room temperature for 72 hours in the same way. At this time, the film compound was labeled ZC-2. Every film contained chemical compound was rinsed with deionised water, dried, and cut into 2 cm × 2 cm. They were identified by X-ray diffraction (XRD: RINT 1500, Rigaku Corporation) using the Cu-Kα radiation. Also, every film was embedded in epoxy resin and polished, thereafter its cross-section was observed by scanning electron microscope (SEM: JED-2300, JEOL Ltd.)

2.2 Membrane potentials

In Fig. 2, the film with the chemical compounds was inserted between cell A and B. Both cells were filled with KCl aqueous solution. The concentration of KCl in cell A was set at 0.1M and that in cell B was ranged from 0.001 M to 1 M. After that, measurement of membrane potential was initiated. The membrane potential value 10 minutes after immersion of the films was adopted by using potentio/galvanostat (Model 1287, Solartron Corporation). As comparative samples, two kinds of films were prepared. One was semipermeable membrane without any chemical compounds; the other was the film indicating cationic permselectivity (N-112, DuPont Corporation). The membrane potentials of these films were similarly measured. The chloride ion's transport numbers of all the films were led by Equation (1).

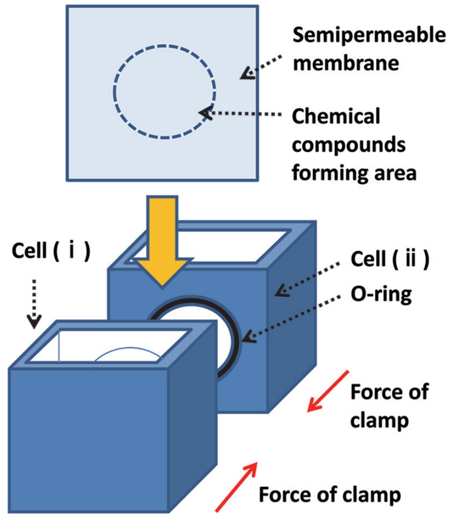

Fig. 3 Chemical compound film making equipment

3. Experimental Results and Discussions

3.1 Film analyses

Figure 4 shows the appearance of the film and SEM micrograph of the film cross-section. The chemical compounds were formed into the semipermeable membrane. The thickness of the chemical compounds in the film was about 50 μm. The chemical compounds were closely formed in the film.

Figure 5 shows the XRD results of the chemical compounds. Zinc hydroxide [$Zn(OH)_2$: Joint Committee for Powder Diffraction Standards (JCPDS) No. 38-0385] and zinc oxide [ZnO: JCPDS No. 36-1451] were detected in ZC-1, whereas zinc hydroxychloride [$Zn_5(OH)_8Cl_2H_2O$: JCPDS No. 07-0155] was detected in ZC-2. From the above results, it was found that ZC-1 was a film composed of zinc hydroxide and zinc oxide and that ZC-2 was a film consisting of zinc hydroxychloride.

Figure 6 shows the pH–pCl diagram of zinc.[6)] The pH in 0.5M $ZnCl_2$ is about 5.4, and pCl is about 0.0. Meanwhile the pH in 0.1 M NaOH is about 13, pCl is infinitesimal. As a result, the pH in the center of the semipermeable membrane was presumed between 12 and 13, pCl was between 0.0 and 1.0 in 1st step in **Table 1** due to the liquid diffusion. Thus the condition of the semipermiable membrane is indicated by dotted circle in Fig. 6. This is why zinc hydroxide and zinc oxide were formed in the semipermiable membrane. On the other hand, the pH in 2nd step in Table 1 is about 4.7 and pCl is −0.6, which is indicated by a closed circle in Fig. 6 similarly. It is apparent that zinc hydroxychloride is stable in the condition, so the mixture compounds were transformed into zinc hydroxychloride.

At first, we attempted to form zinc hydroxychloride in the 1st step by making the semipermeable membrane environment suitable for stabilization of zinc hydroxychloride. However, we could not obtain any film because the chemical compound was formed outside the semipermeable membrane. Therefore, the sample preparation process was divided into two steps in which the chemical compound formed in the semipermeable membrane was to be transformed into zinc hydroxychloride. As a result, the aimed compound membrane could be obtained.

3.2 Membrane potentials

Figure 7 shows the relation between the membrane potentials and C_B/C_A in Equation (1). The inclination of the approximate straight line

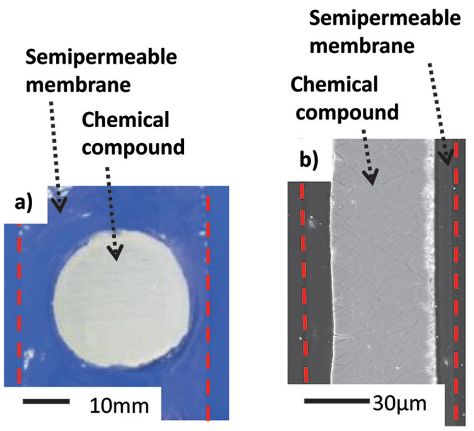

Fig. 4 a) Appearance of ZC-2 b) ZC-2 cross-section

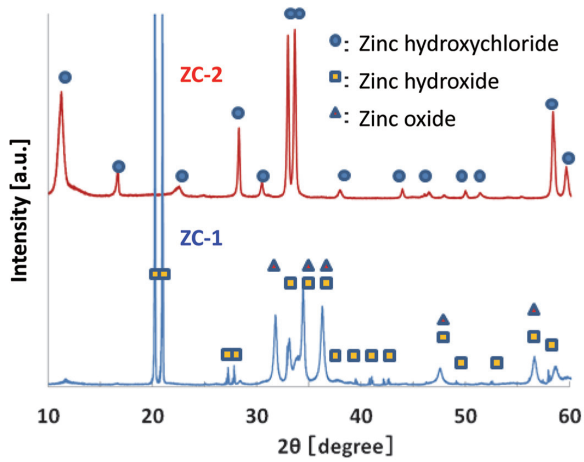

Fig. 5 XRD results

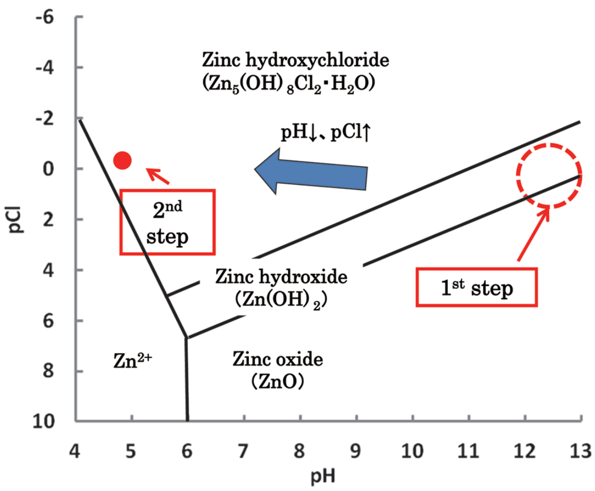

Fig. 6 pH-pCl diagram of zinc [6]

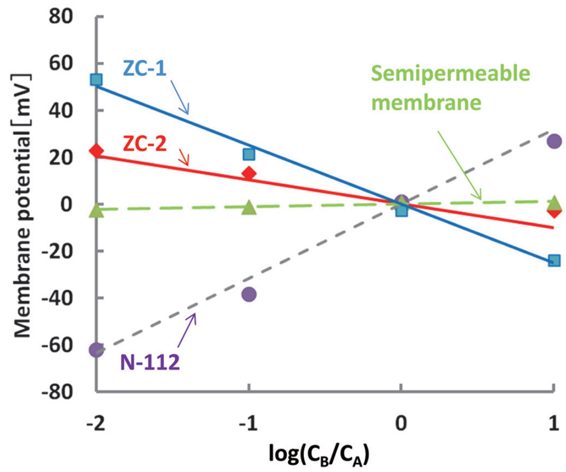

Fig. 7 Relationship between (C_B/C_A) and membrane potentials

Table 1 Transport numbers of films

	Sample name	Transport number of Cl^- (t^-)	Ion permselectivity
Samples	Zinc hydroxide and zinc oxide (ZC-1)	0.70	Anionic
	Zinc hydroxychloride (ZC-2)	0.58	Anionic
Comparative samples	Semipermeable membrane	0.49	Unshown
	N-112	0.23	Cationic
	Iron (III) oxide [4]	0.96	Anionic

was −25 for ZC-1 and −10 for ZC-2. Therefore, it was found that both ZC-1 and ZC-2 are films having an anionic permselectivity. In contrast, the inclination of the approximate straight line for the semipermeable membrane was near zero, the semipermeable membrane had no ion permselectivity. On the other hand, the inclination of the approximate straight line for N-112 was 31, indicating that N-112 had a cationic permselectivity. Thus, it was confirmed that the results of the membrane potential measurement are valid and that the semipermeable membrane does not influence ion permselectivity. Thus, it can be observed that both zinc hydroxide–zinc oxide mixture and zinc hydroxychloride show anion permselectivity in KCl solution.

Table 1 shows the average transport numbers of Cl^- for the films, together with the transport number for iron oxide [III] given in the literature.[4] Zinc hydroxychloride's transport number was 0.58, smaller than mixture of zinc hydroxide and zinc oxide at 0.70, which indicated zinc hydroxychloride's anionic permselectivity was weak. On the other hand, the transport number of iron oxide [III] was 0.96. Since zinc hydroxychloride has a transport number smaller than that of iron oxide [III] and can hardly pass Cl^-, there is a possibility that it serves as an effective barrier to the permeation of corrosive factors.

In the future, it is necessary to clarify which of the properties of zinc hydroxychloride contributes to the corrosion resistance of zinc-coated steel sheets the most by analyzing its electrical resistance and density.

4. Conclusion

1) The film containing zinc hydroxychloride was prepared, and its membrane potential was measured.
2) The ion permselectivity of zinc hydroxychloride film was anionic, and its transport number of chloride ion was 0.58.

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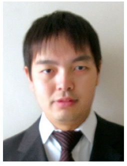
Mamoru SAITO
Surface Treatment Research Lab.
Steel Research Laboratories
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

Nobuyuki SHIMODA
Senior Researcher
Surface Treatment Research Lab.
Steel Research Laboratories



Kohei TOKUDA
Researcher
Surface Treatment Research Lab.
Steel Research Laboratories