Ion Selective Permeability of Rust Layers on Low Alloy Steels under the Chloride Ion Existence

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The ion selective permeability of the rust on carbon steel and Fe-Co and Fe-Ni low alloy steel was investigated by measurement of membrane potential to evaluate the characteristics of the rust layer on low alloy steels. These steels were selected as testing materials because they were thought to be basic alloys of weathering steels for the use in coastal environments. A rust film was formed on two kinds of low alloy steels (Fe-Co and Fe-Ni steel) by corrosion cycle tests that imitated the atmospheric corrosion environment in the seashore. In the case of the carbon steel, the rust layer on it had anion selective permeability. On the other hand, in spite of the rust layer on the carbon steel was anion selective, it was found out that the permeability changed to the cation selective by the result of determining the membrane potential of the rust on Fe -Co low alloy steel. The addition of a few Co was effective for decreasing the corrosion rate, because the rust layer of the cation selective was obstructed the invasion of chloride. The addition of Ni was known to be effective in decreasing corrosion rate of steel, despite their anion selective nature in rust layer. Alternative mechanism other than ion selectivity is required for the explanation of inhibition by Ni. The tendency of the membrane potential measurement of rust layers on all samples formed by corrosion cycle test was same as the case of rust films formed by exposure tests.

Keywords : Low alloy steel, Carbon steel, Ion selective permeability, Rust layer, Atmospheric corrosion

1. Introduction

High corrosion resistance is required for the material to use in the severe corrosion environment. Weathering steel has also been studied as a thing that the process of the corrosion is controlled by a rust film formed in the surface.[1] However, in the severe environment corrosion progresses on the weathering steel as well that has an excellent corrosion resistance in the mild condition. Therefore, the development of the weathering steel that can be used in the seashore environment is a pressing need. Moreover, the development of the low alloy weathering steel which has a little addition alloying element is hoping from the viewpoint of department resources-ization.[2] For the corrosion behavior of the low alloy steel, the study of the analysis[3,5] of the surface rust layer and the potential distribution measurement[6,7] on the surface is reported. The rust analysis on the low alloy steel so far with the form of the rust maintained has been done.[8] The evaluation of ion permeability in the rust layer using membrane potential measurement is effective to examine the corrosion behavior after the rust formation, and then it has been

discussed by many researchers. The membrane potential measurement of a precipitation film was done by Suzuki[9] and Sakashita.[10] The membrane potential measurement was also occurred recently by Miyuki[11] and Kihira[12] as the investigation of the weathering steel. As an artificial rust film was made and a membrane potential was determined in the usual research, the macro structure of a rust film did not have an included characteristic evaluated, either. The authors also reported the ion selective permeability of rust layers considering the structure of the rust.[13,14]

In this paper, the corrosion characteristic of the different low alloy steel (Fe-Co, Fe-Ni low alloy steel) designed was evaluated by electrochemical method and the ion selective permeability of rust layers formed by corrosion cycle tests and exposure tests for the purpose of the development of low alloy steel to use in the seashore environment.

2. Experimental

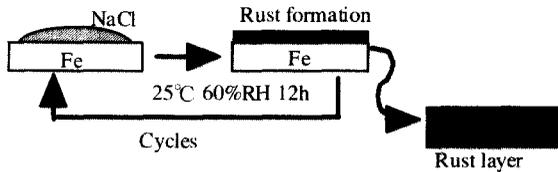Samples are Fe-1mass%Co, Fe-3mass%Co Fe-1mass

Fig. 1. Sample procedure of the rust film in membrane potential measurement.

%Ni and Fe-3mass%Ni low alloy steel. Carbon steels were used as the comparative materials. The preparation of samples was shown in Figure 1. Sample of the size of 20mm x 20mm x t0.02mm was fixed to expose the strip side of the board and then was exposed in the atmospheric that simulated atmospheric corrosion environment in the seashore part. In corrosion cycle tests, 0.8ml of 0.5%NaCl solution was dropped on the surface of the sample and was kept at 25°C and the relative humidity of 60% RH for 12 hours. In each cycle test, rinsing was done after this process. This cycle test was repeated, and a rust film was made. There is no accumulation of NaCl because rinsing is being done in every cycle. It was repeated at least 20 cycles until all the steel material samples became rust. After the sample of only the rust where the substrate metal does not remain was formed, it was fully submitted for the membrane potential measurement (15) after the rinsing. Furthermore, after the corrosion cycle tests, polarization curves were measured in 0.5 mass% NaCl solution method was carried out in Na2SO4 solution. Dry weight was measured in each cycle, and corrosion rate was determined from the weight increasing per unit volume. The membrane potential of rust layers formed on steels by exposure tests in coastal environment was also measured.

3. Results and Discussion

3.1 Corrosion rate and electrochemical behavior of rusting steels

Weight gain of the low alloy steels during corrosion cycle tests was shown against the cycle number in Figure 2. The corrosion rate of both two low alloy steels (Co and Ni additive alloy) was decreased comparing with the case of the carbon steel. Therefore, Co and Ni may be effective alloy element on corrosion resistance under atmospheric corrosion environment of the sea side.

From the result of the bare steel (Figure 3 (A)), Co and Ni addition had the effect of decreasing the anodic dissolution for the low alloy steel surface, so corrosion resistance of the Co and Ni additive alloy was higher than carbon steels for the initial stage. Polarization curve of 3 mass% Co additive alloy in NaCl solution after corrosion
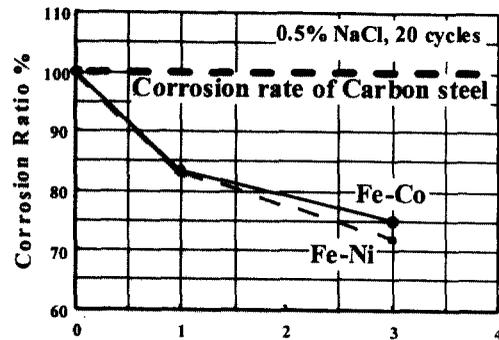

Fig. 2. Corrosion rate of low alloy steels(Fe-Ni, Fe-Co) under corrosion cycle tests. The corrosion rate of the carbon steel is made 100%
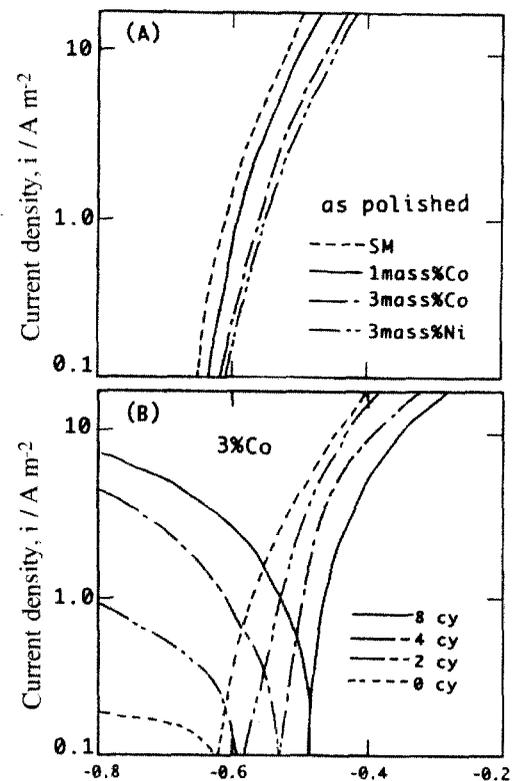

Fig. 3. Polarization curves of bare steel and Co and Ni additive alloy(A), and 3 mass % Co additive alloy in NaCl solution after corrosion cyclic tests (B).

cycle tests was also indicated in Figure 3 (B). As the cycle number increased, the cathodic current increased. Increasing of cathodic current was attributed to reduction of the rust formed on the low alloy steel during the corrosion cycle tests. It was shown that increasing of the cathodic current was occurred by the reduction of β-FeOOH because β-FeOOH was main phase in the rust layer. However, the formation of rust layer on the steel accelerated the cathodic reaction, decreased the anodic

reaction. The formation of the rust layer made structural barrier on the surface of steel, and disturbed the mass transfer through the layer.

3.2 Ion selective permeability of rust layers

Figure 4 shows the membrane potential of rust layer on carbon steel and low alloy steels against the concentration ratio of both KCl solution. From these results of membrane potential, the rust layer on carbon steel had anion selective permeability. The ion selective permeability of the rust composition component showed the anion permeability of the rust film. It shows that fixed charge is plus that the ion selective permeability of the rust film is anion selectivity. It can be thought with the benefit that surface charge is plus in the rust film which has a lot of pore. It is suitable in the neutral chloride solution from the interpretation (16) of N. Sato that oxy -hydroxide of iron is anion selectivity as well. It was indicated that the rust film with a form maintained on carbon steel was anion selective permeability using membrane potential measurement of the film.

Rust layers on the carbon steel was anion selective, however, it changed to the cation selective permeability as the result of determining the membrane potential of the rust on Fe -3mass% Co low alloy steel as also shown in Figure 4 that contained the result of the carbon steel. The addition of a few Co was effective for decreasing the corrosion rate, because the rust layer of cation selective obstructed the invasion of chloride.

However, the corrosion rate of the Fe-Ni low alloy steel was about 70% in comparison with the case of the carbon steel, anion permeability was shown from the fructification of the membrane potential measurement of the rust layer formed on the Fe-3mass% Ni in Figure 4. It was confirmed that it is partly being taken into the iron spinel oxide in 2plus in the case of Ni (bivalence ; Ni(II)) by the analysis

of the rust film by XPS (17). As it is different from the case of Co, it can think that this is the cause which ion selective permeability is different from. Because the corrosion rate of the Ni addition steel is small in comparison with the carbon steel, the effect on the corrosion protection of the Ni addition is not the ion selective permeability system of the rust. It can be thought that it attributes in effect on ion transfer retardation through the rust or the Ni addition play the role as the element which obstructs the anodic dissolution as the above mentioned. It is important that the efficiency of Ni addition to iron is made clear detail.

The material characterization technique with the form of the rust maintained as rusting in the corrosion test was established through this measurement, and it was effective in the characterization of the rust. This procedure can be applied even if it faces a rust film formed in natural environments and a rust film on other alloy system.

3.3 Ion selective permeability of rust layers formed by exposure tests

Figure 5 shows results of membrane potential measurement of rust layers formed by the corrosion cycle test and exposure test on the carbon steel and low alloy steels. In the case of the carbon steel and Ni additive alloy, the rust layer on alloys had anion selective permeability. Therefore, chloride was passed through the rust layer also formed by exposure tests on the carbon steel to the metal surface and corrosion was progressed. The addition of a few Co was effective for decreasing the corrosion rate, because the rust layer of cation selective which was also observed in Figure 5 was obstructed the permeation of chloride ion. The tendency of the membrane potential measurement of rust layers on all samples formed by corrosion cycle test was same as the case of rust films formed by exposure tests. The corrosion cycle test was effective for the study on the rust layer of low alloy

Fig. 4. Membrane potential of the rust layer formed by the corrosion cycle test on the carbon steel and low alloy steels.

Fig. 5. Membrane potential of rust la yers formed in wet / dry environment.

weathering steels.

The material characterization technique with the form of the rust maintained as rusting in the exposure test was established through this measurement, and it was effective in the characterization of the rust film. This procedure can be also applied on the characterization of a rust film formed in natural environments and a rust film on other alloy system.

4. Conclusions

1) It was found out by the physical analysis that Co existed in FeOOH in the rust layer as the trivalence, and Ni was mainly contained in the spinel oxide.

2) Co and Ni were effective alloy element on corrosion resistance under atmospheric corrosion environment of the sea side. Increasing of cathodic current in the polarization curve was attributed to reduction of the rust formed on the low alloy steel during the corrosion cycle tests. Furthermore, it found out the suppressing effect of rust layer in the anodic reaction.

3) The addition of Co of a small quantity changes the selectivity from anion to cation selectivity, so corrosion resistance improves. For the dependence toward the ion selectivity of the Co addition volume, it was found out that it did not appear remarkably. The ratios of the corrosion rate decrease by the Ni addition, though the rust film on the Fe-Ni low alloy steel shows anion selective permeability.

4) The tendency of the membrane potential measurement of rust layers on all samples formed by corrosion cycle test was same as the case of rust films formed by exposure tests.

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