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THE ROLE OF RUSTS IN CORROSION AND CORROSION PROTECTION OF IRON AND STEEL

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Abstract: The processes of atmospheric corrosion of iron and steel and the properties of corrosion products (rusts) are modeled based on a quantitative evaluation of the chemical reactions pertaining to corrosion to elucidate the conditions with which corrosion-protective rust films form. in the initial stage of corrosion, in the rusts, the pH of the aquatic system is maintained at 9.31 owing to an equilibrium with iron (II) hydroxide and the rate of air-oxidation at this pH is very fast, and that dense, self-repairing rust films form, protecting the underlying iron and steel. However, after corrosion stops, the rust film deteriorates due to the dissolution and shrinkage by aging, and the deteriorated rust film separates the anode and cathode reaction products (Fe2+ and OH- ions) to cause crevice corrosion .The air-oxidation of iron (II) in anode channels without the presence of OH- ions results in strongly acidic solutions (pH 1.41), causing acid-corrosion. It is proposed that good catalysts (e.g. copper (II) and phos-phate ions) accelerate the air-oxidation at low pH, delaying the crevice- and acid-corrosion stages. Further, it is argued that iron compounds with negative charges due to the non-stoichiometric proportions of the lattice oxide ions and metal ions (solid oxoanions of iron) exhibit stable cation-selective permeability even with a drop in pH. Rust films including such compounds would stop the passage of aggressive anions and act to protect iron and steel.

Keywords: Atmospheric corrosion processes, Oxidation-reduction reactions

Abstrak: Proses korosi atmosferik pada besi dan baja serta sifat-sifat produk korosi (karat) dimodelkan berdasarkan evaluasi kuantitatif dari reaksi kimia yang berkaitan dengan korosi untuk menjelaskan kondisi terbentuknya lapisan karat yang bersifat melindungi dari korosi. Pada tahap awal korosi, pada karat, pH sistem air dipertahankan pada 9,31 karena adanya kesetimbangan dengan besi (II) hidroksida dan laju oksidasi udara pada pH ini sangat cepat, dan lapisan karat yang padat dan dapat memperbaiki diri sendiri terbentuk, melindungi besi dan baja yang mendasarinya. Namun, setelah korosi berhenti, lapisan karat memburuk karena pelarutan dan penyusutan akibat penuaan, dan lapisan karat yang memburuk memisahkan produk reaksi anoda dan katoda (ion Fe2+ dan OH-) yang menyebabkan korosi celah. Oksidasi udara dari besi (II) dalam saluran anoda tanpa adanya ion OH- menghasilkan larutan yang sangat asam (pH 1,41), menyebabkan korosi asam. Diusulkan bahwa katalis yang baik (misalnya ion tembaga (II) dan fosfat) mempercepat oksidasi udara pada pH rendah, menunda tahap korosi celah dan korosi asam. Lebih lanjut, dikatakan bahwa senyawa besi dengan muatan negatif karena proporsi non-stoikiometri dari ion oksida kisi dan ion logam (oksoanion padat besi) menunjukkan permeabilitas selektif kation yang stabil bahkan dengan penurunan pH. Lapisan karat yang mengandung senyawa tersebut akan menghentikan perjalanan anion agresif dan bertindak untuk melindungi besi dan baja.

Kata kunci: Proses korosi atmosferik, Reaksi reduksi oksidasi

Introduction

Corrosion is defined in different ways, but the usual interpretation of the term is "an attack on a metallic material by reaction with its environment". The concept of corrosion can also be used in a broader sense, where this includes attack on nonmetallic materials"), and several definitions of corrosion have been given and some of them are reproduced below [1]:

1. Corrosion is the surface wastage that occurs when metals are exposed to reactive environment
2. Corrosion is the result of interaction between a metal and environments which results in its gradual destruction.
3. Corrosion is an aspect of the decay of materials by chemical or biological agents. Copper has excellent electrical and thermal conductivity and is often used in heating and cooling systems. The presence of corrosion products decreases the heating efficiency of the equipment, making necessary procedures of descaling and cleaning in acid solutions.

Additions of certain organic compounds to the cleaning solutions protect the metal from the destructive effect of the acid on such equipments. Among the acid corrosion inhibitors for copper, some nitrogen, sulphur or, oxygen containing compounds reduce copper dissolution due to the chelating action of heterocyclic molecules. "Weathering steels" have been developed with the idea that rusts formed by corrosion shield the metal from environments and inhibit further corrosion. This is represented by the saying that "rusts stop rusting", which stands for the inhibition of corrosion by the corrosion products. It is considered that well working weather-ing steels require little maintenance, and recently extensive appli- cation of weathering steels is planned for bridges, buildings, and in other construction. However, there are cases where rusts accelerate corrosion as suggested by the saying that "rusts invite rusting" where rusts are not corrosion-protective but corrosion-promoting. The loss of the protective abilities of rusts is very unfavorable and fatal for weathering steels. To improve the performance and reli- ability of weathering steels, it is important to elucidate the role of rusts in corrosion and to ensure the development of protective properties of rusts in a wide range of environmental conditions.

1.1 Corrosion And Development Of Protective Rust Films

Formation of iron(II) and hydroxide ions by corrosionIron and steel surfaces are covered with a thin oxide layer of $Fe3O4$ or $c\text{-}Fe2O3$ from the very beginning due to exposure to air. In the presence of water and oxygen, metallic iron is thermodynamically unstable as apparent from the Pourbaix diagram (4), and corrosion proceeds according to the electrochemical mechanism as shown in Fig. 1. Iron is oxidized at the anode to dissolve $Fe2+$ ions, dissolved oxygen is reduced at the cathode to form $OH-$ ions, and these are combined to deposit iron(II) hydroxide so- lid, $Fe(OH)2(s)$, when the solubility is exceeded

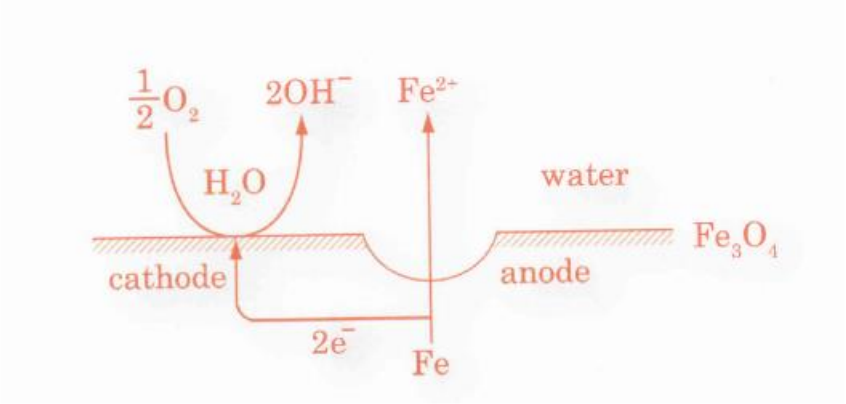

Fig. 1. Electrochemical mechanism of corrosion of iron

1-2 Passive Oxide Films

The idea of corrosion protection by corrosion products can be traced back to the discovery of "passivation" of iron, where iron keeps its metallic luster without corroding in concentrated nitric acid solutions. Dipping iron in chromate solutions or the application of appropriate anodic potentials to iron also leads to passivation. Passivation of iron requires strongly oxidizing environments, and passivity is attributed to protective oxide films formed by oxidation of iron as first proposed by Faraday. In passiv-ation of iron, iron is oxidized instantaneously in strongly oxidizing conditions to form oxides containing iron (III) with very low solubilities, and this oxide is assumed to be directly formed in close connection with the crystal structure of the metal [5]. This little soluble oxide film isolates the metal surface from corrosive environments and prevents further corrosion. When a film in an oxidizing environment is imperfect or broken, iron exposed to the solution through the film defects is immediately turned into the little soluble oxides containing iron(III) at the defect sites and the film is repaired. As a result, the passive oxide film is not merely a static physical barrier that is formed only once at a certain stage of passivation, but it is a self-maintaining dynamic barrier that is constantly repaired and renewed.

Methods

1-3 Characterization Of Rusts And Rust Formation

In atmospheric corrosion, steels in ordinary structures, not necessarily in strongly oxidizing environments, corrode to form rusts. These rusts are generally coarse, porous, and flaky substances without the properties necessary to shield the steel from environ- ments, and so do not have protective and self-maintaining proper- ties like passive oxide films**.**

Corrosion resistance in weathering steels indicates the forma- tion of special types of rusts, and studies have been made of the characteristics and properties of rusts. It has been reported that. a-, b-, c-FeOOH, c-Fe2O3, Fe3O4, and amorphous oxyhydroxides are included in the rusts [6-11]. It is assumed that small rust parti- cles are packed densely to form a tightly adherent film that acts as a barrier protecting the steel from further corrosion, and nano-sized a-FeOOH and amorphous oxyhydroxides of iron(III) are con- sidered protective [7,8]. However, rust components show some solubility to water, and if a protective rust film forms and further corrosion stops, then without the supply of iron ions and hydroxide ions due to corrosion, the protective film deteriorates with time forming defects by dissolution. The rust film is not permanently maintained as protective, and corrosion will start again through the defect sites. Rusts providing just a mechanically dense and tightly adherent film do not seem adequate to develop into a long-lasting film to shield iron and steel from water and oxygen.

Results and Discussion

1-4 Purpose Of This Investigation

In this investigation, it is pointed out that for rusts to develop into a long- lasting protective film, constant self-repairing of the film by fusing particles together, by filling up defect spaces, or by other means is necessary, like the passive oxide film that is self- maintained by repairing defects. The atmospheric corrosion of iron and steel is composed of several reactions, e.g., formation of hydroxide ions at the cathode, dissolution of iron(II) and alloying metal(II) ions at the anode, air-oxidation of iron(II) to iron(III), iro- n(III) hydroxo-complex formation, precipitation and dissolution of iron(III) hydroxide, magnetite, and ferrites, transformation of these compounds to rusts by aging, ion adsorption on rusts, and other reactions. As a result, an atmospheric environment that brings about the corrosion of iron and steel can be regarded to constitute an aquatic system.

This paper studies the role of rusts in corrosion and corrosion protection of iron and steel by analyzing the related chemical reactions in aquatic systems based largely on the author's previous work. In the previous individual works, the chemical reactions themselves were the interest of the studies, and the relation to the corrosion of iron and steel was explored only superficially. However, the investigation in this paper aims at the elucidation of corrosion phenomena by integrating the author's previous works and offers insights into the mechanism of corrosion and the role of rusts in corrosion and corrosion protection. The results obtained advance the knowledge of corrosion and can be applied to develop weathering steels.

Conclusion

1-5 Observed Results For Rust Formation

"The Research Group of Rust Chemistry" (Chairman: Prof. T. Ohtsuka) of the Japan Society of Corrosion Engineering has carried out the characterization of rusts formed on weathering steels and inspected sites of corrosion in weathering-steel bridges. The results of these activities as well as the findings for the corrosion of iron and steel obtained so far (6.11] can be summarized as,

- **a.** In wet environments containing chlorides, iron and steel corrode forming rusts with brownish colors.
- **b.** Occasionally rust surfaces are stained yellow and it appears that "rust fluids" have leaked out, and the new yellow rust formed is called "flowing rust". The "flowing rust" indicates that corrosion is not a static process, but that dynamic changes occur during rusting.
- **c.** Rusts develop into a layer structure with repeating dense and coarse layers.
- **d.** The chloride ions are concentrated at layer boundaries, the most notably at the rust/substrate interface.
- **e.** The application of wet pH-test paper to rust surfaces exposed by removing the surface layers clearly indicates the presence of acidic ($pH < 3$) and alkaline ($pH > 10$) regions.
- **f.** On steels constantly exposed to water, rusts keep growing and finally detach as flakes or even as slabs at the substrate/rust interface.

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