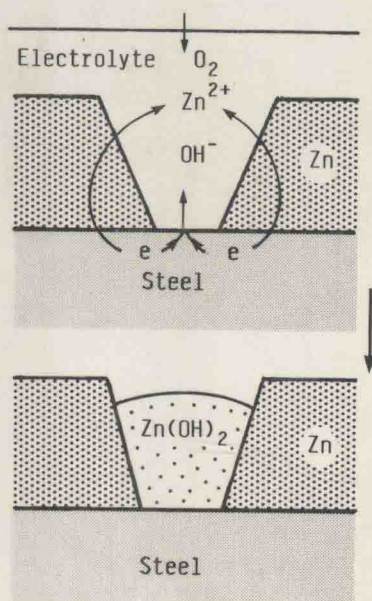


CORROSION- RESISTANT COATINGS TECHNOLOGY



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Corrosion-Resistant Coatings Technology

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Preface

In the past 20 years, technology for corrosion-resistant coatings has been advanced by the improvement of surface treatment processes and the development of more corrosion-resistant materials. New coating control systems and surface analytical equipment, as well as progress in the underlying science itself, have contributed to the advancement.

Reporting the current status of corrosion-resistant coatings, this book was written for students, engineers, and others who are interested in corrosion protection. The scope of this book includes the selection and application of coatings used widely in natural environments, including metallic, inorganic, and organic coatings. It does not cover ceramic coatings and linings, organic linings, or coatings used at high temperatures or in particular environments.

The emphasis in this book is on the protective abilities of coatings for various environments, particularly environments characterized by moisture and water. The corrosive species covered are the same as those battled by engineers: moisture, water, pollutants, and caustic substances. This book draws on much of the excellent research already done on corrosion resistance.

Corrosion-resistant coatings are exposed predominantly to natural environments. Since natural atmospheric conditions are always fluctuating, it is not easy to evaluate atmospheric elements, particularly moisture in the atmosphere. In 1958, P. J. Sereda of the National Research Council of Canada introduced the consideration of time-of-wetness on the basis of critical humidities shown by W. H. J. Vernon. The pioneer research by P. J. Sereda and Herbert Guttman forms the basis of this book. Following their work, I have introduced the concept of corrosion rate of metal during wet period to evaluate the protective abilities of coatings under natural atmospheric conditions.

The book is divided into six chapters. In the first, the principles of corrosion protection by coatings are described on the basis of electrochemistry. Chapters 2-6 describe the major types of coatings. Sacrificial metal coatings are covered in Chapter 2, noble metal coatings are in Chapters 3 and 4, inorganic coatings in Chapter 5, and organic coatings in Chapter 6. Each coating is described based on its classification in the corrosion protection principles in Chapter 1. Chapters 2-6 include sections concerning practical mechanisms of corrosion protection by coatings, production methods and main products, and protective ability and environment. In additional sections, the applications of coatings are discussed.

I am deeply indebted to Professor L. L. Faulkner of Ohio State University and Professor S. Brad of City College of City University of New York for providing me with the opportunity to write this volume.

This book contains many figures, tables, and data, for which I acknowledge many associations, societies, companies, and many authors for permission, especially the National Association of Corrosion Engineers, the American Society for Testing and Materials, The Electrochemical Society, Inc., The Institute of Metals, American National Standards Institute, the American Society for Metals, The Metallurgical Society of AIME, The Metal Finishing Society of Japan, the Japan Association of Corrosion Control, The Iron and Steel Institute of Japan, and the Japan Society of Corrosion Engineering.

I am grateful also to many friends for their contributions. I would especially like to thank Professor Henry Leidheiser, Jr., of Lehigh University, who led me to the field of corrosion-resistant coatings and always provided encouragement and advice. I am grateful to Charles E. Cannon, who made grammatical corrections in my English and gave me much advice. I would also like to acknowledge the following people for their assistance: Dr. Herbert E. Townsend of Bethlehem Steel Corp., Dr. Takeshi Adaniya of Nippon Kokan K. K., Dr. Hidejiro

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Finally I wish to thank my wife, Michiko, who typed my manuscript, and my son, Kazumichi, and my daughter, Nao, who always encouraged me.

Ichiro Suzuki

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1

Principles of Corrosion Protection by Coatings

Other than metals such as gold and platinum which are discovered already in the metal state in their natural environments, many widely used metals are unstable in the atmosphere. These unstable metals are produced by reducing ores artificially; therefore, they will return to their original ores or to similar metallic compounds when exposed to the atmosphere. For example, metallic iron is oxidized to ferric oxyhydroxide in a thermodynamically stable state; that is, iron in the higher level of free energy is changed to lepidocrocite, γ - FeOOH , in the lower level:



$$\Delta G^\circ = -81 \text{ kcal/mole} \quad (1.2)$$

This behavior of a metal in a natural environment is called corrosion. The role of a coating is to prolong the time until rust forms on the substrate, as shown in Fig. 1.1. The service life of a coating depends on the properties of the coating material and on the degree of aggressiveness of the environment. Therefore, the selection of coating

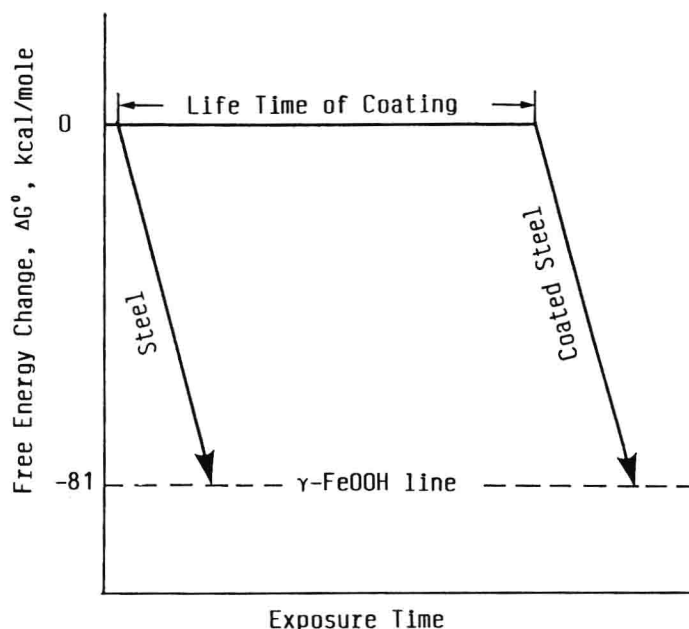


Fig. 1.1 Role of corrosion-resistant coating.

materials for metals used in various environments is a most important engineering process. Recent progress in corrosion science has made coating technology more accessible.

In this chapter, the electrochemical principle of corrosion protection by coatings is described, because metal corrosion almost always proceeds electrochemically in the natural environment.

1.1 PROTECTIVE ABILITIES OF COATINGS

The protective ability of a coating requires the isolation of a base metal from the atmosphere. The isolating capacity of a coating, that is, the service life of a coating, depends on the physical quantity and the chemical properties of the coating layer. The former is the thickness of the coating layer. The latter determines the durability of a coating material in a particular environment that is, the corrosion resistance of a metal coating and the stability of its organic and inorganic compounds. The durability of a coating material must be

greater than that of the base metal or it must be maintained by some means. And, moreover, the ability to protect the base metal beneath the coating layer—with its original pore and crack, or with a defect resulting from mechanical damage and pitting corrosion—is often required of a coating layer.

Commonly used corrosion-resistant coatings are classified into five categories on the basis of electrochemical principles:

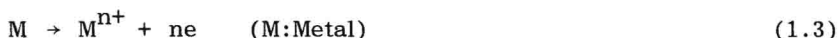
1. EMF control protection
2. Cathodic control protection
3. Anodic control protection
4. Mixed control protection
5. Resistance control protection

Theories of these protective abilities of coating can be explained by the mechanism of the corrosion cell.

1.1.1 Corrosion Cell

In the natural environment, the corrosion of most metals occurs and proceeds electrochemically. Namely, the corrosion cell is formed on a metal surface in an atmosphere in which oxygen and water are present, as shown in Fig. 1.2. The electrochemical reactions in the corrosion cell are written in general form:

Anodic reaction



Cathodic reaction

in acidic solution



in neutral and alkaline solutions



The mechanism of the corrosion cell can be represented in Fig. 1.3 by using the Evans diagram [1,2]. In the Evans diagram, the cathodic current is expressed in the same direction as the anodic current.

In Fig. 1.3, E_a shows the single potential for metal | metal-ion equilibria at the anode, and E_c shows the single potential for $H_2 | H^+$, or for $O_2 | OH^-$ equilibria at the cathode. The single potential is given by the Nernst equation. That is,

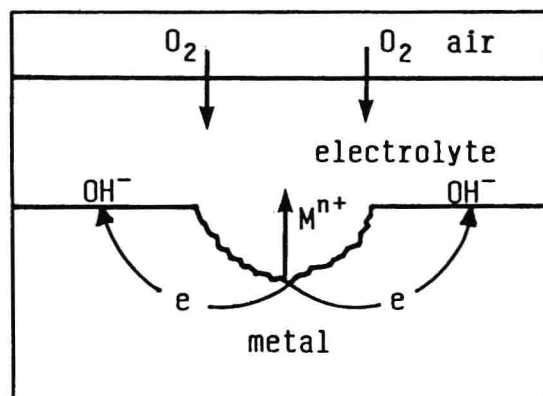
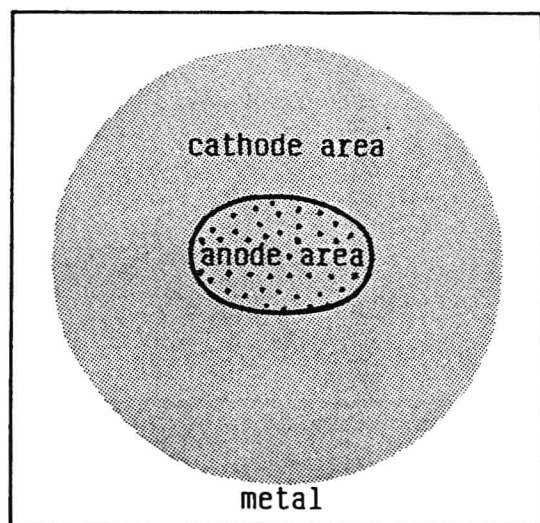


Fig. 1.2 Structure of the corrosion cell.

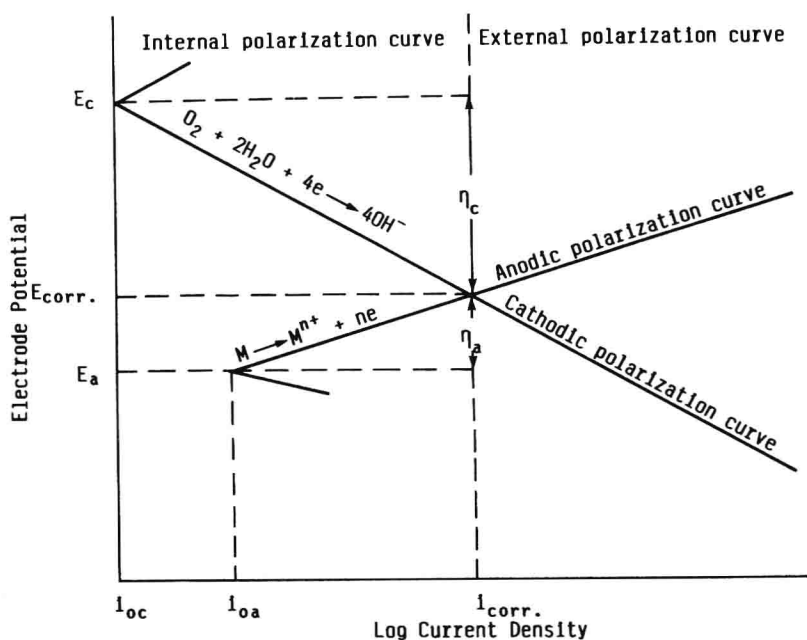


Fig. 1.3 Mechanism of the corrosion cell.

$$E = E^0 + \frac{RT}{nF} \ln a \quad (1.6)$$

where E is the single potential, E^0 is the standard single potential, R is the gas constant, T is the absolute temperature, n is the charge on an ion, F is the Faraday constant and a is the activity of the ion. E is equal to E^0 when a is 1. The standard single potential is E^0 and it shows the degree of activity of, for example, metal and gas.

Table 1.1 shows the standard single potential of various metal and nonmetal reactants. The arrangement of metals in order of electrode potential is called the electrochemical series. The more negative the single potential is, the more active the metal is. When the corrosion cell circuit is formed, that is, when the electromotive force ($E_c - E_a$), is supplied, the current flows between the anode and the cathode. The anodic electrode potential is shifted to the noble direction; the cathodic electrode potential is also shifted, but to the less noble direction. The behaviors of these electrode potentials are called anodic and cathodic polarization. Each reaction-rate curve ($E - i$ curve) is also called an anodic or cathodic polarization curve.

Table 1.1 Standard Single Potentials, E^0 (V, SHE, 25°C)

Active		Inert	
Electrode	E^0	Electrode	E^0
Li Li ⁺	-3.01	Mo Mo ³⁺	-0.2
Rb Rb ⁺	-2.98	Sn Sn ²⁺	-0.140
Cs Cs ⁺	-2.92	Pb Pb ²⁺	-0.126
K K ⁺	-2.92	H ₂ H ⁺	0
Ba Ba ²⁺	-2.92	Bi BiO ⁺	+0.32
Sr Sr ²⁺	-2.89	Cu Cu ²⁺	+0.34
Ca Ca ⁺	-2.84	Cu Cu ⁺	+0.52
Na Na ⁺	-2.71	Rh Rh ²⁺	+0.6
Mg Mg ²⁺	-2.38	Hg Hg ⁺	+0.798
Th Th ⁴⁺	-2.10	Ag Ag ⁺	+0.799
Ti Ti ²⁺	-1.75	Pd Pd ²⁺	+0.83
Be Be ²⁺	-1.70	Ir Ir ³⁺	+1.0
Al Al ³⁺	-1.66	Pt Pt ²⁺	+1.2
V V ²⁺	-1.5	Au Au ³⁺	+1.42
Mn Mn ²⁺	-1.05	Au Au ⁺	+1.7
Zn Zn ²⁺	-0.763	O ₂ OH ⁻	+0.401
Cr Cr ³⁺	-0.71	I ₂ I ⁻	+0.536
Fe Fe ²⁺	-0.44	Br ₂ Br ⁻	+1.066
Cd Cd ²⁺	-0.402	Cl ₂ Cl ⁻	+1.356
In In ³⁺	-0.34	F ₂ F ⁻	+2.85
Tl Tl ⁺	-0.335	S S ²⁻	-0.51
Co Co ²⁺	-0.27	Se Se ²⁺	-0.78
Ni Ni ²⁺	-0.23	Te Te ²⁺	-0.92

The intersection of anodic and cathodic polarization curves shows the corrosion potential, $E_{\text{corr.}}$, and the corrosion current, $i_{\text{corr.}}$. Thus, the anodic and cathodic electrodes react at the same rate in the corrosion process.

The polarization curves in the current density range $< i_{\text{corr.}}$ are called internal polarization curves and those in the current density range $> i_{\text{corr.}}$ are called external polarization curves. The external polarization curve can be determined by sweeping the electrode potential from the corrosion potential to the anodic or cathodic direction. On the other hand, the internal polarization curve cannot be measured directly by the electrochemical technique since it is impossible to pick up the current separately from the anode and the cathode, which exist in an electrode. The internal polarization curves are determined by the analysis of metallic ions dissolved and oxidizer reaction.

The difference in potential between $E_{\text{corr.}}$ and E_a or between $E_{\text{corr.}}$ and E_c is called anodic overpotential or cathodic overpotential and is expressed with η_a or η_c . That is,

$$\eta_a = E_{\text{corr.}} - E_a \quad (\eta_a > 0) \quad (1.7)$$

$$\eta_c = E_{\text{corr.}} - E_c \quad (\eta_c < 0) \quad (1.8)$$

$\eta_a/i_{\text{corr.}}$ or $\eta_c/i_{\text{corr.}}$ represent the anodic or the cathodic reaction resistance.

The corrosion reaction starts as soon as the cell circuit is formed. That is,

$$E_c - E_a = |\eta_c| + \eta_a + i_{\text{corr.}} R \quad (1.9)$$

where R is the resistance of electrolyte between the anode and cathode. Thus, the electromotive force of a corrosion cell is dissipated as the corrosion current passes through three processes: the anodic process, the cathodic process, and the transit process in the electrolyte.

In general, when the electrode is polarized, the overpotential η , observed, is composed of the activation overpotential η^a , and the concentration overpotential η^c (Fig. 1.4). That is,

$$\eta = \eta^a + \eta^c \quad (1.10)$$

The activation overpotential η^a results from the potential energy barrier to be overcome for a charge to cross the electrical double

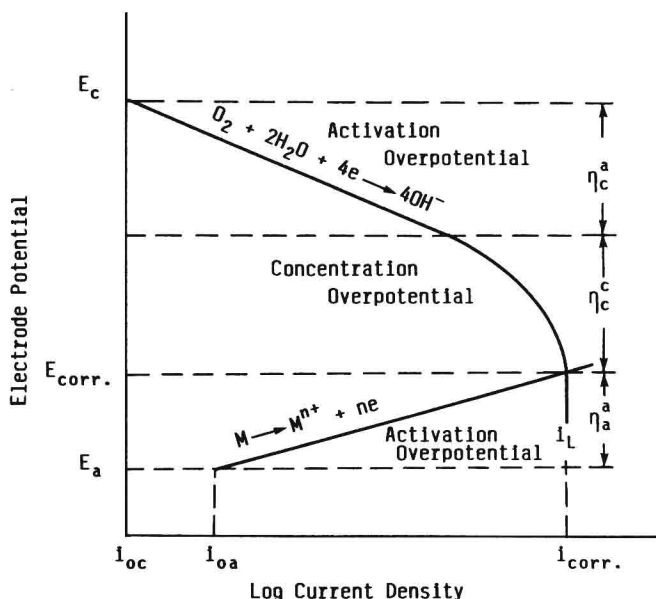


Fig. 1.4 Activation and concentration overpotentials in typical corrosion process.

layer at the interface (i.e., $M \rightarrow M^{n+} + ne$) and is given as follows:

In the anodic reaction

$$\eta_a^a = \beta_a \log \frac{i_a}{i_{oa}} \quad (1.11)$$

$$\beta_a = 2.3 \frac{RT}{\alpha nF} \quad (1.12)$$

In the cathodic reaction

$$\eta_c^a = \beta_c \log \frac{i_c}{i_{oc}} \quad (1.13)$$

$$\beta_c = - \frac{2.3RT}{(1 - \alpha)nF} \quad (1.14)$$

where η_a^a and η_c^a are the activation overpotentials in the anodic and cathodic reactions, β_a and β_c are the anodic and cathodic Tafel coefficients, α is the transfer coefficient, i_a and i_c are the anodic and cathodic current densities, and i_{oa} and i_{oc} are the exchange current densities of anodes and cathodes. The energy transfer factor, α , indicates the degree of contribution of electrical energy for the activation energy in the electrode reaction ($0 < \alpha < 1$). In most cases, α is 0.3–0.7. The exchange current density, i_{oa} or i_{oc} , is the flux of charge that passes through the electrical double layer at the single-equilibrium potential, E_a or E_c . Other factors have been mentioned already. Eqs. (1.11) and (1.13) are called the Tafel equation. There is a linear relationship between η^a and $\log i_a$ or i_c . Tafel coefficient β_a or β_c is the slope, $d\eta^a/d(\log i_a \text{ or } i_c)$, of the polarization curve, so that β is one of the important factors that control the corrosion rate.

Generally, the activation overpotential controls the electrode reaction at the low reaction rate. The cathodic reaction $2H^+ + 2e \rightarrow H_2$ is, in the acid solution, one of the processes controlled by the activation overpotential. Table 1.2 shows hydrogen overpotentials of various metals. The activation overpotential varies with the kind of metal and the electrolytic condition. In most cases, metal dissolution and metal-ion deposition are controlled by the activation overpotential.

Therefore, the anodic overpotential, η_a , is usually given by Eq. (1.11). That is,

$$\eta_a = \beta_a \log \frac{i_a}{i_{oa}} \quad (1.15)$$

On the other hand, the concentration overpotential, η_c , becomes the controlling factor in the electrode reaction at high reaction rate. In this case, the electrode reaction is controlled by mass transfer process, that is, the diffusion rates of reactive species. Namely, according to the diffusion-layer concept [4], the diffusion current, i , is given as follows:

$$i = \frac{nFD(C - C_0)}{\delta} \quad (1.16)$$

where i is the current density, D is the diffusion coefficient, C is the concentration of reactive species in the bulk solution, C_0 is the concentration of reactive species at the interface, and δ is the thickness