*The Inhibitive Behavior of the Fluoride Ion and the Destruction of Its Protective Film in the Corrosion of Magnesium in Neutral Solutions**

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Fluoride ions accelerate the corrosion rate of aluminum in a manner quite similar to that of other halide ions.[1] Iron is corroded in a dilute solution of potassium fluoride as well as in a solution of potassium chloride, but its corrosion is suppressed in a solution of potassium fluoride more concentrated than 0.8 N.[2,3] The inhibitive action of chromate ions on the corrosion of zinc is considerably strengthened by the addition of fluoride ions.[4,5] Now, in the case of magnesium, the fluoride ion has been known to be a good inhibitor and to exhibit a somewhat different behavior from that of such other ionic inhibitors as the chromate, bichromate and nitrate ions.[6] In this paper, a mechanism for the formation of protective films by the fluoride ions and their destruction by corrosive ions will be presented on the basis of electrochemical kinetics.

Experimental

Materials. — The magnesium metal used was obtained from the E. Merck Chemical Company, Darmstadt, Germany, in the form of a ribbon 3.18 mm. in average width, 0.26 mm. in average thickness, and 99.93% pure. The impurities, as found by spectrographic analysis,[7] are shown in Table I.

TABLE I. IMPURITIES IN MAGNESIUM (%)

Fe	Mn	Cu	Al	Si	Ca	Zn
0.017	0.014	0.005_1	0.002_0	0.003_5	0.0003_7	<0.01

Sn	Sr	Ni	Cr	V	Ti	Pb
<0.005	<0.005	<0.001	<0.001	<0.005	+	−

After a magnesium specimen was cut in an appropriate length, the connection to the leading wire was sealed completely by paraffin so as not to come in contact with the corroding reagent. The effective surface area of magnesium acting as an electrode was determined by a micrometer microscope, considering its surface to be flat enough, or its roughness factor to be unity, and disregarding the edge effect in the course of reaction. The magnesium was cleaned by acetone just before the measurements.

Polarization Characteristics of Magnesium in Various Solutions. — The stationary potentials of magnesium at various external current densities in several corrosion media are shown in Fig. 1. The anodic polarization curves in corrosive media, such as the aqueous solutions of potassium chloride and potassium bromide, are almost horizontal, while those in solutions containing inhibitive reagents, such as potassium nitrate, potassium chromate and potassium fluoride, are displaced towards nobler potentials and have steeper slopes; especially in the case of potassium fluoride, the curve is quite vertical and the anodic current is markedly retarded.

On the other hand, all the cathodic polarization curves are very similar to one another.

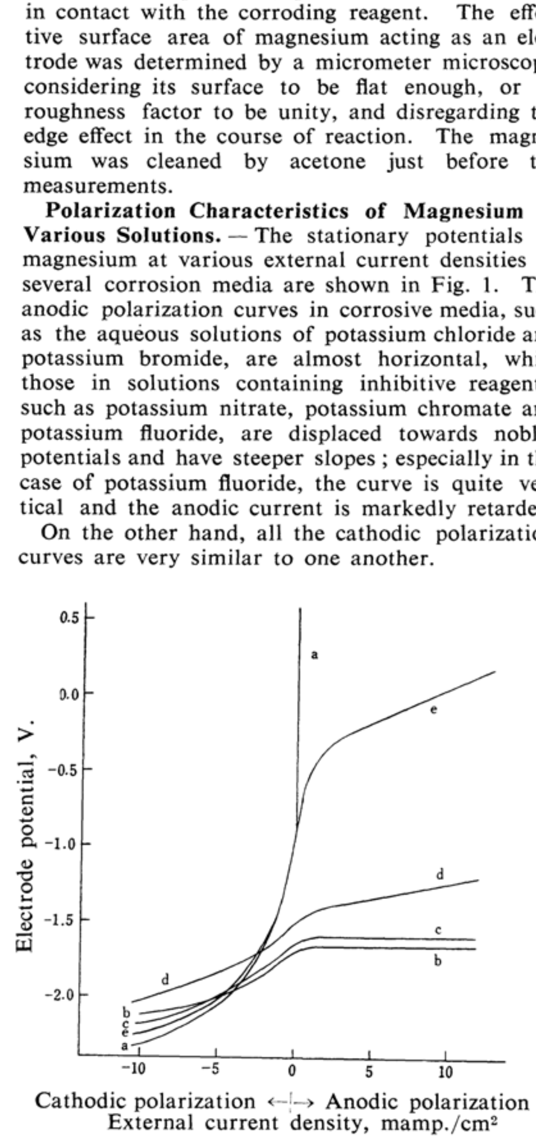

Fig. 1. Polarization characteristic curves of magnesium in 0.1 N aqueous solutions of various electrolytes at 20°C.

(a)	KF	(d)	KNO_3
(b)	KCl	(e)	K_2CrO_4
(c)	KBr		

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* Corrosion Reaction of Magnesium. Part XIV. The previous report appeared in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1461 (1958).

1) M. Izuyama and Y. Hayakawa, *J. Electrochem. Soc. Japan*, **29**, 873 (1961).

2) A. W. Chapman, *J. Chem. Soc.*, **1930**, 1546.

3) U. R. Evans, "The Corrosion and Oxidation of Metals, Scientific Principles and Practical Applications," Edward Arnold Publishers, London (1960), p. 176.

4) U. R. Evans, ibid., p. 185.

5) C. V. King, E. Goldschmidt and N. Mayer, *J. Electochem. Soc.*, **99**, 423 (1952); C. V. King and E. Hilmer, ibid., **101**, 79, (1954); C. V. King and E. Rau, ibid., **103**, 331 (1956).

6) G. Wada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 279 (1954).

7) N. Oda, S. Tuno and M. Idohara, *J. Electrochem. Soc. Japan*, **30**, 350, E-111 (1962).

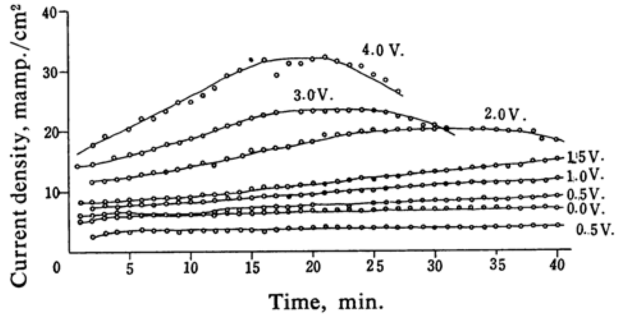

Fig. 2. Variations of anodic current densities with time at various potentials in a 0.001 N KCl solution at 20°C.

The Formation of Fluoride Films.—The inhibitive action of the fluoride ion on the corrosion of magnesium has been attributed to the formation of fine protective films composed of insoluble magnesium fluoride on the magnesium surface. Concerning this, the following facts were found in this experiment: a) 4.9 μg./cm² of the fluoride ion was deposited on the surface when magnesium was anodically polarized at 2 V. in a 0.1 N solution of potassium fluoride for 15 min., using a 0.1 N calomel electrode as the reference; b) 69.0 μg./cm² of the fluoride ion was also deposited when the magnesium was left alone in the same solution for 40 days. Provided that these amounts of deposited fluoride ions form homogeneous films of magnesium fluoride over the surface, their thicknesses would be about 280Å in the case of a) and about 4000Å in the case of b). In the experiment, the determination of small quantities of fluoride ion was carried out by the method of spectrophotometric titration using sodium alizarin monosulfonate.[8]

The quantity of electricity accumulated in the film during the 15 min. period was calculated to be about 0.03 coul./cm² from the observed current density-time relation,[9] while the theoretical quantity of electricity necessary to form the film in the case of a) is equal to about 0.025 coul./cm². Therefore, the current efficiency is nearly equal to unity for the formation of the magnesium fluoride film. Moreover, the result in the case of b) indicates that the magnesium fluoride film still continues to grow spontaneously by the diffusion of charged particles through the film, even in the natural, or externally unpolarized, state.[10]

The Destruction of Magnesium Fluoride Films by Corroding Reagents.—Figures 2 and 3 show the time variations in the potentiostatic external current densities observed at various electrode potentials in the corrosive solutions, where magnesium had previously been covered with a magnesium fluoride film by treating it in a 0.1 N potassium fluoride solution under the same conditions as in the case of a) mentioned above.

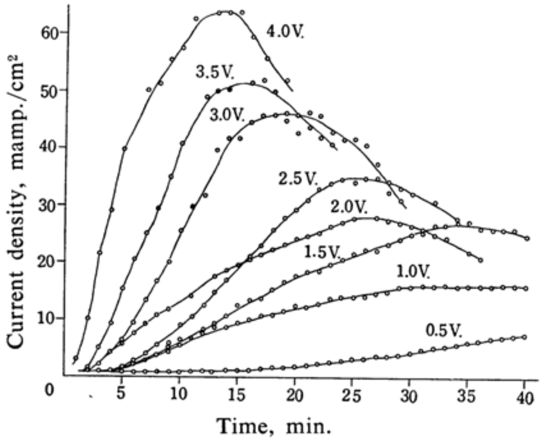

Fig. 3. Variations of anodic current densities with time at various potentials in a 0.001 N KCl+0.1 N KF solution at 20°C.

In any case, the current density increases with time at the first stage, reaches a maximum, and then gradually begins to decrease. At the stage of increase, the destruction or the stripping of the magnesium fluoride film mainly occurs; at the stage of decrease, on the other hand, perhaps the surface is covered by the products of corrosion, the hydroxide of magnesium.

When fluoride ions coexist with chloride ions in the solution, the current density is rather larger than when the chloride ion alone is present. The fluoride ion itself must have the power to promote corrosion like other halide ions if magnesium fluoride were not insoluble.

Discussion

The Mechanism of Film Rupture.—As the fine film of magnesium fluoride covering the surface is quickly destroyed and stripped off by the attack of corrosive ions, the bare area of

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[8] W. P. Pickhardt, *Anal. Chem.*, **34**, 863 (1962).

[9] The electric current was quite large at the instant when magnesium was brought into contact with a 0.1 N potassium fluoride solution and afterwards reduced abruptly to an extremely low value.

[10] Since the densities of magnesium fluoride and metallic magnesium are 3.17 and 1.74 g./cm³, the atomic densities with respect to magnesium are 5.0×10^{-2} and 7.2×10^{-2} g.-atom/cm³ respectively. Accordingly, there occurs as much as a 44% expansion in the volume of magnesium with the transformation from the metallic state into a magnesium fluoride film.

the surface, without the film, expands and, accordingly, the apparent current density increases. However, since the products of the corrosion, such as magnesium hydroxide soon begin to interfere with the contact of the bare area with the corroding reagent, the apparent current density begins to decrease after reaching its maximum. Now, if the fractions of three kinds of surface areas, namely the bare and those covered with magnesium hydroxide and magnesium fluoride, are denoted by s_1, s_2 and s_3 respectively, and if the true current densities at a certain potential, E, on the respective areas are denoted by i_1, i_2 and i_3, the following relations can be established, where I represents the averaged current density over the total surface:

$$s_1+s_2+s_3=1 \tag{1}$$

$$\frac{\mathrm{d}s_1}{\mathrm{d}t}+\frac{\mathrm{d}s_2}{\mathrm{d}t}+\frac{\mathrm{d}s_3}{\mathrm{d}t}=0 \tag{2}$$

$$I=s_1i_1+s_2i_2+s_3i_3 \tag{3}$$

$$\left(\frac{\partial I}{\partial t}\right)_E=i_1\left(\frac{\partial s_1}{\partial t}\right)_E+i_2\left(\frac{\partial s_2}{\partial t}\right)_E+i_3\left(\frac{\partial S_3}{\partial t}\right)_E \tag{4}$$

Judging from the nature of the surface, $i_1 \gg i_2$, and $i_3 \approx 0$. Therefore, Eq. 4 may be written as:

$$\left(\frac{\partial I}{\partial t}\right)_E=-i_1\left(\frac{\partial s_3}{\partial t}\right)_E-(i_1-i_2)\left(\frac{\partial s_2}{\partial t}\right)_E \tag{5}$$

In the cases as shown in Figs. 2 and 3, $s_1=s_2=0$ and $s_3=1$ at the beginning of the reaction, but s_1 has fluctuating values between zero and unity in the midst of the reaction and afterwards converges again to zero. Consequently, the slopes of the nearly straight lines appearing before and after the peaks in Figs. 2 and 3 are approximately expressed by Eqs. 6 and 7 respectively, and the condition corresponding to the maximum point is expressed by Eq. 8.

$$\left(\frac{\partial I}{\partial t}\right)_E\simeq-i_1\left(\frac{\partial s_3}{\partial t}\right)_E \quad \text{Initial stage} \tag{6}$$

$$\left(\frac{\partial I}{\partial t}\right)_E\simeq-(i_1-i_2)\left(\frac{\partial s_2}{\partial t}\right)_E \quad \text{Final stage} \tag{7}$$

$$-\left(\frac{\partial s_3}{\partial t}\right)_E\simeq\left(\frac{\partial s_2}{\partial t}\right)_E \quad \text{Maximum point} \tag{8}$$

The intrinsic anodic polarization characteristic curves for the respective kinds of areas are schematically shown in Fig. 4, where i_1 is, of course, by far the largest among the three throughout the whole range of the potential. The Tafel relation holds on the bare area as long as the potential is low, but i_1 gradually fails and reaches a saturation value which is controlled by the diffusion at the higher potentials.[11] The electrode potential on the mixed surface of the areas with different natures is denoted by E in Fig. 4, as "a compromise potential."[13]

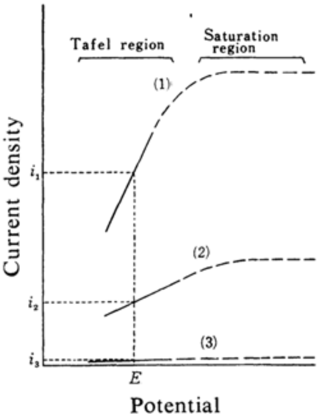

Fig. 4. Schematic diagram for the anodic polarization characteristic curves of different surface areas.
(1) Bare
(2) Covered with $Mg(OH)_2$
(3) Covered with MgF_2

Now, when the logarithms of the slopes of the initial and the final stages, $\log(\partial I/\partial t)_E$, in Figs. 2 and 3 are polotted against the potential, straight lines are obtained, as Fig. 5 shows. Therefore, recognizing that the potentials are high enough for i_1, i_2 and i_3 to be already saturated and hardly to vary with the potential, as can be seen in Fig. 4, the following relations can be derived:

$$R_\mathrm{F}=\frac{A_\mathrm{F}}{i_1}\exp\frac{\alpha_\mathrm{F}\boldsymbol{F}E}{\boldsymbol{RT}} \tag{9}$$

$$R_\mathrm{O}=\frac{A_\mathrm{O}}{i_1-i_2}\exp\frac{\alpha_\mathrm{O}\boldsymbol{F}E}{\boldsymbol{RT}} \tag{10}$$

where $R_\mathrm{F}\equiv-(\partial s_3/\partial t)_E$, i.e., the rate of the destruction of the magnesium fluoride film; $R_\mathrm{O}\equiv(\partial s_2/\partial t)_E$, i.e., the rate of the fomation of the magnesium hydroxide film; A_F and A_O are the characteristic constants; α_F and α_O are the transfer coefficients,[14] and $\boldsymbol{F}$ is the Faraday constant. Table II shows the transfer coefficients calculated from Fig. 5.

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[11] The anodic polarization curve of magnesium in a potassium chloride solution as shown in Fig. 1 is nearly horizontal. This was obtained by the steady-state method. If determination were performed on a fresh surface of magnesium by the rapid method, the curve should have a somewhat steeper slope in quite the same way as in the case of aluminum.[12]

[12] G. Okamoto, T. Morozumi and F. Arai, *J. Electrochem. Soc. Japan*, **27**, 437 (1559).

[13] U. R. Evans, Ref. 3, p. 893.

[14] M. Maeda, "Denkyoku no Kagaku (Chemistry of Electrodes)," Gihodo Series 12, Tokyo (1961), p. 102.

TABLE II. TRANSFER COEFFICIENTS OF THE POTENTIAL CURVES ALONG THE REACTION COORDINATES IN THE REACTIONS OF THE MgF_2-FILM DESTRUCTION, α_F, AND OF THE $Mg(OH)_2$-FILM FOMATION, α_O

Solution	α_F	α_O
0.001 N KCl	2.8×10^{-2}	0.41×10^{-2}
0.001 N KCl×0.1 N KF	2.3×10^{-2}	2.1×10^{-2}

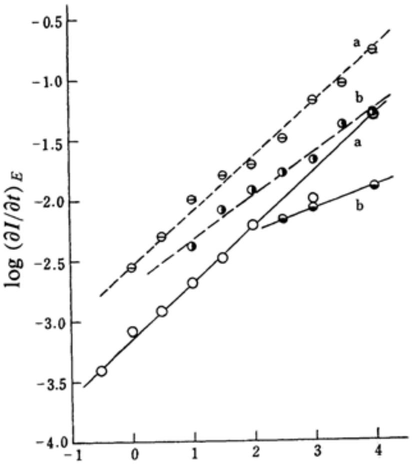

Fig. 5. Variations of $\log(\partial I/\partial t)_E$ of (a) the initial and (b) the final stages with the potential of magnesium.
—— 0.001 N KCl solution
---- 0.001 N KCl+0.1 N KF solution

In the reaction of the magnesium fluoride-film destruction, α_F's have values similar to each other irrespective of the presence of fluoride ions in the solutions, while in the magnesium hydroxide-film formation, the α_O's in the different solutions are quite different from each other. In the former reaction, a step which the existing ions do not seriously influence would be rate-determining, although it is not clear whether the reaction proceeds through a mechanical stripping-off of the film or through a chemical oxidation of fluoride ions. The films of magnesium hydroxide formed by the latter reaction, on the contrary, would all be different because of the adsorption of different ions.

The Activation Energy of the Destruction Reaction of the Magnesium Fluoride-film and That of the Cathode Reaction on the Same Surface.—The apparent activation energy of the reaction of the magnesium fluoride-film destruction at 0.5 V. in a 0.001 N KCl+0.1 N KF solution in the temperature range between 15 and 40°C was found to be nearly 19 kcal./mol. by plotting the logarithms of $(\partial I/\partial t)_E$ at the initial stage against the reciprocals of the temperature. This value is only one-fourth of the electron affinity of fluorine, 3.94 eV.[15] and seems to be too low if the destruction reaction involves a real electrochemical oxidation of fluoride ions. Therefore, it is probable that the destruction of the film is forced to occur through a mechanical stripping caused by the invasion of the corrosive reagent between the film and the metal. On the other hand, the apparent activation energies of the cathode reaction on the surface covered with magnesium fluoride, which had been formed beforehand in a 0.1 N potassium fluoride solution at 2.0 V. for 15 min., could be obtained from the temperature variations of the cathodic current density at -2.1V.; they are 3.0 kcal./mol. in a solution of 0.1 N potassium fluoride and 3.3 kcal./mol. in one KF 0.001 N KCl+0.1 N KF respectively.

As it could be ascertained that neither the reduction of Mg^{2+} ions nor the deposition of magnesium occurred at all through the magnesium fluoride film in the cathode reaction, it may be said, taking the very low values of both apparent activation energies into account, that the electric conduction through the film is not ionic but electronic. However, when the metal is polarized anodically, electricity is conducted through the magnesium fluoride-film neither by electrons nor by ions, in spite of the fact that the magnesium fluoride-film can grow by means of the diffusion of certain ions through the film, as has been mentioned. Thus the rectifying phenomenon by the magnesium fluoride-film can be recognized when the solution contains no other anions but fluoride ions.

Summary

Fluoride ions exhibit an anomalous inhibitive ability against the corrosion of magnesium; this may be attributed to the formation of a fine film of insoluble magnesium fluoride. This film conducts the cathodic current fairly well, but it conducts the anodic current not at all, as far as it is not destroyed. The cathode reaction through the magnesium fluoride film has a low apparent activation energy because of its electronic conduction, while, when magnesium is anodically polarized, the film is no longer electron-conductive and still permits to a lesser extent the diffusion of any other charged particles; consequently, this is a kind of rectifier in a solution containing potassium fluoride alone.

If a solution contains chloride ions in addition to fluoride ions, the matter is quite

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[15] "Kagaku Benran," Ed. by Chem. Soc. Japan, Maruzen, Tokyo (1952), p. 635.

different and fluoride ions rather promote the corrosion, like other halide ions. When magnesium, the surface of which has previously been covered with magnesium fluoride is anodically polarized in a solution containing only chloride ions or containing fluoride ions as well as chloride ions, the film soon begins to be destroyed at the initial stage, the bare area of high conductivity appears, and then the surface is gradually again covered with the bulky products, magnesium hydroxide, at the later stage. The destruction of the magnesium fluoride film may occur through a mechanical process regardless of the presence of fluoride ions.

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