北海道大学工学部研究報告
第105号（昭和56年）

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 105 (1981)

Corrosion of Aluminum-Copper Alloy and Inhibition Action of Benzotriazole, Tolyltriazole and Hydroquinone in Sodium Hydroxide Solutions

Takenori NOTOYA* and Tatsuo ISHIKAWA*

(Received March 31, 1981)

Abstract

The corrosion rates of an aluminum-copper alloy (2024, Super Duralumin) in sodium hydroxide solutions of seven different concentrations were determined gravimetrically at 30℃. The influence of three organic compounds, hydroquinone (HQ), benzotriazole (BTA) and Tolyltriazole (TTA), on the corrosion behavior of the aluminum-copper alloy was investigated in a concentration range from 0.01 to 0.1 mol/l of sodium hydroxide solutions. The corrosion of the alloy was found to be strongly dependent on the pH level of the alkaline solutions, and additions of these compounds resulted in a decrease of pH of the solution and thus leading to the decrease of its corrosion rates. The corrosion tests using a solution of constant pH (=12.8) showed that the inhibition efficiency increased with the increasing concentration of the compounds and the maximum inhibition efficiencies of HQ, BTA and TTA at a concentration of 0.1 mol/l were 40, 13 and 16 %, respectively in 0.1 N NaOH solutions. The inhibition mechanism was discussed in relation to the nature of the corrosion product layer formed on the metal surface.

1. Introduction

Although aluminum and aluminum alloys are highly resistant to corrosion in neutral solutions, they dissolve in both acidic and alkaline solutions. Benzotriazole (BTA, 1. 2. 3- 1. H-benzotriazole) and tolyltriazole (TTA, 5-methyl-1. H-benzotriazole) are widely used and the most effective corrosion inhibitors for copper and copper base alloys in various environments.[1] Hardly any information is available on the corrosion inhibition effect of BTA and TTA on other metals, such as aluminum and its alloys in acid or alkaline solutions, although the effect of certain chelate-forming inhibitors for aluminum have been studied.[2]

This paper describes the corrosion behavior of aluminum-copper alloy and the inhibitive effect of BTA and TTA on corrosion behaviors of the alloy in sodium hydroxide solutions, and the results obtained were compared with that of hydroquinone

* Department of Metallurgy

(HQ), which affords a certain degree of protection to aluminum corrosion in sodium hydroxide solutions.[3]

2. Experimental

Chemical structure of BTA, TTA and HQ are shown in Figure 1. Plates of aluminum-copper alloy (2024, Super Duralumin) were supplied by Nittetsu Curtain Wall Co, Ltd. Chemical composition of the aluminum alloy is as follows; Cu 4.56, Si 0.04, Fe 0.17, Mn 0.45, Mg 1.13, Zn 0.01, Cr 0.01 Ti 0.01, Zr 0.01 and Al remainder. The aluminum alloy was extruded at a rate of 2 m/min. at 400℃ and heat treatment was conducted at 500 ± 5℃ for 1 hour followed by water-quenching. Corrosion test specimens were cut to the size of 30 X 20 X 5 mm. Then the specimens were annealed at 500℃ for 1 hour. The surface preparation included mechanical polishing with # 600 SiC paper and degreasing with aceton. The specimens were weighed and totally immersed in 100 ml NaOH solution in the presence and absence of the organic inhibitors for periods of 1 to 6 hours. After the corrosion test the specimens were withdrawn from the corrosive medium and were treated with a mixture of 10 % chromic acid and 1 % phosphoric acid[4] to remove the black corrosion product layer formed on the surface during corrosion, and rinsed in distilled water, dried and weighed. BTA and TTA used are commercially available inhibitors of Cobratec-99 and Cobratec-100, respectively. They were supplied by Sherwin-Williams Company. HQ used is an analytical grade reagent from Wako Chemicals Co, Ltd.

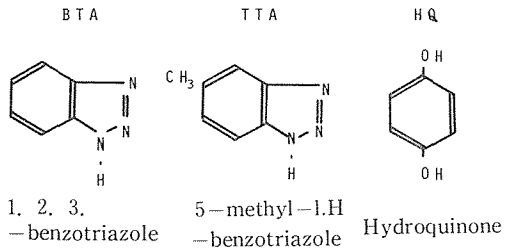


Figure 1 Organic compounds used as inhibitors

3. Results and Discussion

3. 1. Corrosion by NaOH solutions

Figure 2 shows the weight loss of the aluminum-copper alloy as a function of immersion period in sodium hydroxide solutions at seven different concentrations from 0.01 to 1 N at 30℃ under stationary conditions. Within 2 hours the weight loss increases linearly with time and NaOH concentration, i. e., the corrosion rate was constant for the initial period of immersion. Then the weight loss decreased with the immersion period showing a curvature until its maximum value is reached. This tendency was more pronounced at lower concentrations because of the depletion of hydroxyl ions in the solution, which were consumed in the corrosion process. The corrosion reactions of aluminum in NaOH solutions can be described as;

$$Al + NaOH + H_2O \longrightarrow NaAlO_2 + 3/2\ H_2 \quad (1)$$

$$Al + NaOH + 5H_2O \longrightarrow Na^+ + [Al(OH)_4 \cdot 2H_2O]^- + 3/2\ H_2 \quad (2)$$

Table I Corrosion rates in mg/cm². hr at different concentrations of NaOH and temperature.

Concentration of NaOH (N)	Temperature (°C)		
	30	40	50
0.025	1.89	2.82	4.40
0.05	2.89	4.65	6.80
0.1	4.71	7.20	10.91
0.25	7.67	13.30	19.32
0.5	11.33	20.86	31.23
1.0	15.91	29.06	49.00

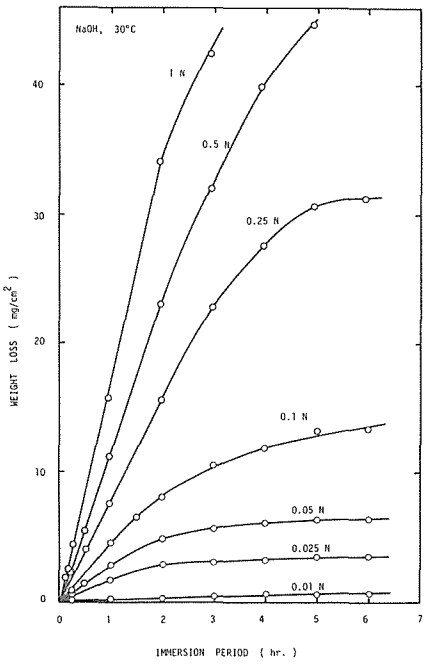


Figure 2 Effect of immersion period on weight loss of 2024 aluminum alloy in NaOH at different concentrations.

Since aluminum hydroxide is precipitated in a pH range of the solution from about 4 to 10,[5] it is considered that no possibility existed to reduce the corrosion rate by oxide and/or hydroxide film formation on the metal surface in such highly alkaline solutions where the pH values were over 12.8.[3] A black corrosion product layer was formed on the surface of the aluminum-copper alloy during the corrosion process, and it became thicker, particularly at higher NaOH concentrations. Because of the solubility difference in the solution among aluminum and its alloy elements, the copper content would be higher in the layer than in the bulk metal.

Caprioglio et al [6] observed that the black layer formed on pure aluminum in NaOH solutions is mainly aluminum oxide containing some particles of metallic aluminum. Although the protecting effect of this layer is limited by its fragility, it has a protective nature to a certain degree. After cleaning the specimens with the chromic -phosphoric acids the surface was smooth and bright at concentrations less than 0.1 N, which is indicative of homogeneous dissolution, while at higher concentrations over 0.1 N a relatively rough surface with fine cracks in the substrate alloy was observed. The cracks may be produced by hydrogen penetration in the bulk alloy during corrosion process and resulted in the so-called hydrogen embrittlement. The corrosion rates, calculated from the slopes of weight loss vs. time relationships at 1 hr immersion period, increases with temperature of the solution, as shown in Table I.

Activation energies for the corrosion process of the aluminum alloy in NaOH solution were estimated from the equation :

$$\log\frac{k_1}{k_2}=\frac{E}{2.303\,R}\cdot\frac{T_2-T_1}{T_1\cdot T_2} \qquad (3)$$

where k_1 and k_2 are the corrosion rates at temperatures of T_1 and T_2, respectively

Table II Activation energy, E, for the corrosion of aluminum-copper alloy in NaOH solutions at six different concentrations.

Concentration of NaOH (N)	Activation energy in Kcal/mol for temperature range		Average Kcal/mol
	30 - 40°C	40 - 50°C	
0.025	7.54	8.94	9.06
0.05	8.96	7.64	
0.1	7.99	8.35	
0.25	10.37	7.50	
0.5	11.50	8.11	
1.0	11.35	10.49	

and E is the activation energy. The values of the activation energy were in a range of 7-11 kcal/mol, as shown in Table II, which are comparable to the data obtained in both NaOH and KOH solutions.[3]

3. 2. Effect of BTA, TTA and HQ

In order to estimate their effect as corrosion inhibitors, BTA, TTA and HQ were added to 0.1 N NaOH solution in a concentration range of 0.01 to 0.1 mol/l of the organic compounds. The dissociation constants of BTA and HQ are $8.2^{(8)}$ and $10.4^{(7)}$, respectively while that of TTA is unknown. Since these compounds act as weak acids, the 0.1 N NaOH solution was neutralized by the addition of the compounds. The change in pH values of the solution with their concentration at 30℃ is illustrated in Figure 3. The figure also shows the increase of the inhibition efficiency with the concentration of the three compounds in a concentration range of 0.01 to 0.1 mol/l. At lower concentrations less than 0.01 mol/l no significant inhibition effect was observed. The inhibition efficiency is expressed as ; $\{(\Delta W_o - \Delta W_i)/\Delta W_o\}$ X100, where ΔW_i and ΔW_o are the weight losses in the solution in the presence or the absence of the compounds, respectively. It is found that the inhibition efficiency of HQ increased almost linearly with its concentration and to attain 97% at 0.1 mol/l while those of TTA and BTA were lower by 20-30% than that of HQ in a concentration of 0.04-0.08 mol/l.

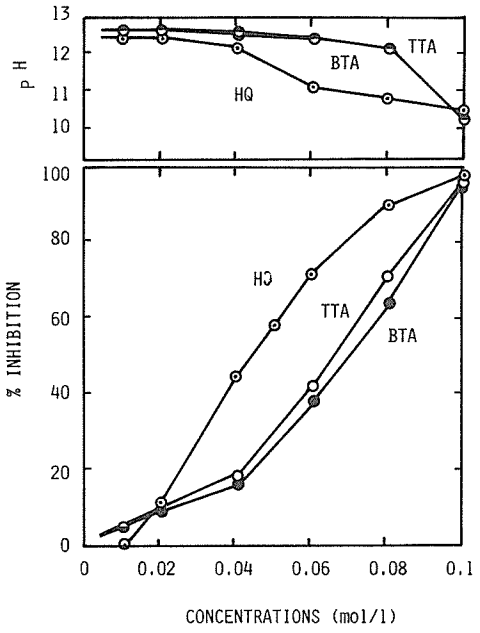


Figure 3 Changes of pH of the solution and inhibition efficiency with concentration of inhibitors. 0.1 N NaOH, 30℃

Hence HQ is a better inhibitor than BTA and TTA. As is indicated in Figure 3, these inhibitive behaviors are in comformity with the pH variation with the concentration of the compounds. Thus, the corrosion of the aluminum-copper alloy is strongly dependent on pH level of the corrosive environments. However, the corrosion product layer formed on the metal surface in the presence of BTA and TTA were firmly attached, in particular at higher concentrations, and were not as easily removed as in the absence of inhibitors or the presence of HQ by the chromic-phosphoric acid treatment. Also, no visible corrosion products were observed in the 0.1 N NaOH solutions saturated with either BTA or TTA within an hour at 30℃. These facts suggest that the additives affect corrosion processes, either by prevention of corrosion or by reducing alkali ions and/or modification of the corrosion product layer to a protective surface layer.

In order to eliminate the pH dependence from the corrosion data, a series of corrosion tests was carried out in a solution of a constant pH (=12.82). The pH level of the solution was adjusted by addition of a small amount of concentrated NaOH solution to the 0.1 N NaOH solution containing the compounds. The corrosion test results are summarized in Table III. The inhibition efficiency of the three compounds in the solution increased in the order of BTA <TTA ≪HQ. Therefore, the inhibition is not simple a function of the pH of the alkaline solution. At lower concentrations, i. e., 0.01 and 0.02 mol/l, both BTA and TTA corrosion acceleration was observed. Even at the highest concentration of 0.1 mol/l, complete inhibition was not obtained and the inhibition efficiency of BTA and TTA was less than 20% and that of HQ was about 40%. The inhibition efficiencies were relatively low compared to the results obtained by O'Neal and Borger.[9] They found inhibition efficiencies of BTA and TTA at concentration levels as low as 10^{-4} mol/l are 21 and 58%, respectively, for 2024 aluminum alloy corrosion in simulated cooling water of pH 8.5 at 50℃. It can be said that BTA and TTA are not suitable inhibitors in these alkaline solutions for practical purposes.

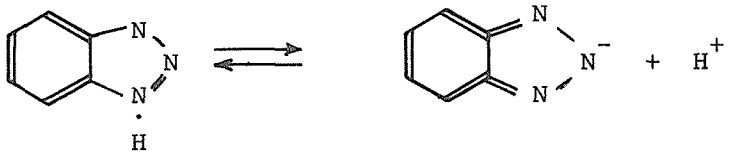
Talati and Modi[3] attributed the inhibition action of HQ in the alkaline solutions

Table III Corrosion test results in NaOH solutions at constant pH* at 30℃ for 1 hr.

Concentration of the additive (mol/l)	Hydroquinone		Benzotriazole		Tolyltriazole	
	Weight loss (mg/cm^2)	% inhibition	Weight loss (mg/cm^2)	% inhibition	Weight loss (mg/cm^2)	% inhibition
0	5.37	----	5.37	----	5.37	----
0.01	4.32	19.5	6.09	- 13.3**	5.98	- 11.4**
0.02	4.26	20.8	5.73	- 6.6**	5.49	- 2.3**
0.04	3.78	29.7	5.21	3.0	5.28	1.8
0.06	3.59	33.0	5.02	6.7	5.07	5.6
0.08	3.28	38.9	4.92	8.4	4.76	11.5
0.10	3.24	39.6	4.68	12.9	4.49	16.3

*pH=12.82 **Acceleration

to chemisorption on to the active sites on the metal surface through the lone pair of electrons of the ketonic oxygen, and thus interfere with the corrosion process. Fagel and Ewing[8] suggested on the basis of ultraviolet absorption spectroscopy that BTA molecule is in the form of a quinoid structure in highly alkaline solutions rather than benzonoid structure, as shown below.



(4)

benzonoid quinoid

It is probable that BTA and TTA molecules having quinoid structures chemisorb on to the active sites on the metal surface, preferentially at copper sites rather than aluminum sites, and inhibit further dissolution. However, the resultant inhibitive effect by addition of BTA and TTA is probably due to strengthening protectiveness to produce polymeric CuBTA or CuTTA complexies in the corrosion product layer. The layer containing CuBTA and CuTTA may provide a more protective configuration than those without these copper inhibitor complexies. Those complexies can be formed by a reaction between BTA or TTA in the solution and copper ions in the corrosion product layer. Although the CuBTA complex film formed on copper in acidic solutions are less protective than that formed in neutral solutions.,[10][11] it actually interferes with the metal dissolution as a physical barrier.

4. Conclusion

The corrosion rate of the aluminum-copper alloy in sodium hydroxide solutions increases with hydroxyl ion concentration and temperature. Three organic compounds, benzotriazole (BTA), tolyltriazole (TTA) and hydroquinone (HQ), exhibit dual functions in alkaline solutions; (i)neutralization of the solution and (ii) corrosion inhibition. The HQ was found to be a better inhibitor than BTA and TTA in the system. Inhibition efficiency of BTA was comparable with that of TTA. Inhibition action of HQ may be attributed to chemisorption on to active sites of the metal surface, while those of BTA and TTA in the corrosion process are mainly due to the modification of the corrosion product layer to the adherent and closely packed layer on the metal surface.

Acknowledgement

The authors express their thanks to Nittetsu Curtain Wall Co, Ltd. for donating the aluminum-copper alloy, and to The Sherwin-Williams Company for the supply of the inhibitors.

References

(1) T. Notoya Boshoku Gijutsu **27** 661 (1978)
(2) Y. Hayakawa and H. Mihara Denki Kagaku **26** 61 and 657 (1968), **32** 23 and 288 (1969)
(3) J. D. Talati and R. M. Modi Br. Corr. J **10** 103 (1975) No. 2
(4) H. H. Uhlig ed. " The Corrosion Handbook " published by John Wily & Sons, Inc., New York p. 41 (1948)
(5) M. Pourbaix "Lectures on Electrochemical Corrosion" plenum press, New York-London p. 59 (1973)
(6) G. Caprioglio, F. Mazza and T. Mussini proceedings of European Symposium on Corrosion Inhibitors, published by Universita Degli Studi di Ferrara p. 419 (1965)
(7) D. D. Perrin "Dissociation Constants of Organic Bases in Aqueous Solutions" Butterworth, London (1965)
(8) J. E. Fagel, Jr and G. W. Ewing J. Am. Chem. Soc. **73** 4360 (1951)
(9) C. O'Neal, Jr. and R. N. Borger Mater. Perform. **15** 9 (1976) No. 2
(10) G. W. Poling Corr. Sci. **10** 359 (1970)
(11) I. C. G. Ogle and G. W. Poling Can. Metal. Quart. **14** 37 (1975)