防蝕工程　第十卷第二期　第 124 ～ 137 頁　民國 85 年 6 月
Journal of Chinese Corrosion Engineering, Vol.10, No.2, PP.124 ～ 137 (1996)

鉻酸鹽轉化鋁合金之微生物腐蝕

楊盛行[a]、顧靜心[a]、林義宗[b]

MICROBIAL CORROSION OF CHROMATED ALUMINUM ALLOYS

SHANG-SHYNG YANG [a], CHING-HSIN KU [a], AND YIH-TSUNG LIN [b]

摘　要

鉻酸鹽轉化鋁合金應用於航空及電子器材以防在溫濕環境下之腐蝕。鋁合金以典型方法經重鉻酸鉀轉化後依ASTM方法在不同水活性測其微生物腐蝕作用。鋁材 AA 1100及鋁合金 AA 6061表面經鉻酸鹽轉化時，比鉻酸鹽轉化鋁合金 AA 2014，AA 2024和 AA 7075對微生物腐蝕具較高保護性。鉻酸鹽轉化鋁合金 AA 7075在水活性0.901下有顯著腐蝕現象，由EDS表面元素分析知腐蝕區鎂含量下降。腐蝕區之金屬氧化物和生物成分對鋁合金局部腐蝕有相乘效果。

關鍵詞：鉻酸鹽轉化，微生物腐蝕，鋁合金，水活性，局部腐蝕，能量分散光度計。

ABSTRACT

Chromate conversion coating on aluminum alloys has been widely used in aerospace equipments and electronic parts to prevent the atmospheric corrosion in mild environmental conditions. Aluminum alloys were chromated with potassium dichromate by the typical method and microbial corrosions were tested according to the ASTM specification under different water activities. Chromate conversion coating on the surfaces of aluminum AA 1100 and aluminum alloy AA 6061 showed higher protective efficiencies than those of aluminum alloys AA 2014, AA 2024, and AA 7075. The chromated film on aluminum alloy AA 7075 had significant corrosion under water activity 0.901, and magnesium content of the corrosion site decreased through the energy dispersive spectrometer analysis. The presence of metal oxides and biological ingredients in the corrosion site acted as the synergistic effects to enhance localized corrosion of aluminum alloys.

Key words: Chromate conversion coating, microbial corrosion, aluminum alloy, water activity, localized corrosion, energy dispersive spectrometer

INTRODUCTION

During the Second World War, the problems of moulding became painfully obvious damage to military equipment used in the tropics area. Work on the prevention of this spoilage went forward rapidly in the USA, Australia, Nigeria, Canada and UK[1]. The specifications were drawn up by interested specialists, scientists, and

a 國立台灣大學農業化學系
Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China
b 中山科學研究院第四研究所
The 4th Department, Chung-Shan Institute of Science and Technology, Lung-Tan, Taiwan 325, Republic of China

technologists who presented their views on the important factors to be used as an indication of the mould resistance of materials. Biodeterioration of metals can be initiated by microbes. Microbial growth adhering to metal surface and liberation of corrosion metabolites as end products could result in the breakdown of protective coating[2].

The deterioration of metal resulting from fungal growth was a very important problem. Because the climate in Taiwan was with high humidity and high temperature, it is apt for the growth of various kinds of fungi on aluminum alloy. Corrosion inhibitors are the chemicals that can reduce the corrosion rate and be used as the retarding catalyst[3,4]. Chromate is the anodic inhibitor and has the oxidation capability. Chromate conversion coating could inert the activity of metal, form a passive film to protect the metal and reduce the corrosion rate[5]. Cr^{6+} ion is converted to Cr^{3+} ion during the conversion coating. Therefore, microbial corrosion of aluminum and chromated aluminum alloys was investigated in this paper by the MIL-STD-810D Test Method with five proposed test organisms[6], one fuel oil contaminated microbe isolated in foreign country, and one fuel oil contaminated microbe isolated in Taiwan[7] at different water activities.

MATERIALS AND METHODS

Test organisms

Aspergillus flavus ATCC 9643, *A. niger* ATCC 9642, *A. versicolor* ATCC 16853, *Chaetomium globosum* ATCC 6205, *Penicillium funiculosum* ATCC 11797, and *Cladosporium resinae* ATCC 22712 were purchased from American Type Culture Collection Centre, Maryland, and were used for corrosion test that were proposed by MIL-STD-810D Test Method[6]. While *Penicillium* sp. AM-F5 was isolated from the fuel oil in Taiwan[7].

Alloy metals

Aluminum AA 1100 and aluminum alloys AA2014, AA 2024, AA 6061 and AA 7075 used in military equipments are obtained from the Chung-Shan Institute of Science and Technology, Taiwan. The specimen dimension is 2.0 × 2.0 × 0.2 cm and the metal composi-

表 1　鋁合金組成份 (%，W W^{-1})
Table 1　Composition of aluminum alloys (%，W W^{-1})

Code number 編號 / Metal 金屬	AA 1100	AA 2014	AA 2024	AA 6061	AA 7075
Cu 銅	0.05-0.2	3.9-5.0	3.8-4.9	0.15-0.4	1.2-2.0
Mg 鎂	-	0.2-0.8	1.2-1.8	0.8-1.2	2.1-2.9
Mn 錳	<0.50	0.4-1.2	0.3-0.9	<0.15	<0.30
Fe 鐵	-	<1.00	<0.50	<0.70	<0.50
Si 矽	<1.00 *	0.5-1.2	<0.50	0.4-0.8	<0.40
Zn 鋅	<0.10	<0.25	<0.25	<0.25	5.1-6.1
Cr 鉻	-	<0.10	<0.10	<0.04-0.35	0.18-0.28
Ti 鈦	<0.05	<0.15	-	<0.15	<0.20
Others 其他	<0.15	<0.15	<0.15	<0.15	<0.15

★ Sum of Fe and Si.

★ Fe和Si總和

tions are presented in Table 1. Specimen was polished with silicon carbide grit No. 240 to remove the aluminum oxide from the surface in all of the tests.

Cultural media and growth conditions

Potato dextrose agar contains (g L^{-1}): potato infusion, 4; glucose, 20; and agar, 20 was used for fungal cultivation. The test organisms were incubated for 7 days at 25 to 30 ℃ for spore formation. Spores were washed with 0.05% Tween 80 from the slant and collected with centrifugation (10,000 x*g*, 20 min) for inhibition and corrosion test [6].

Water activity

Water activity (Aw) was adjusted by the saturation solution of $BaCl_2$ for Aw 0.901 and KCl for Aw 0.842 at 25 ℃[8].

Chromate conversion coating

Aluminum alloy was pretreated with 5% NaOH at 50 ± 5 ℃ for 1 min and washed with deionized water for 1 min, then immersed in 1:1 nitric acid at 25 ℃ for 1 min and then washed with deionized water for another 1 min. After pretreatment, aluminum alloy was chromated in Iridite 14-2 solution [10g Iridite 14-2 (Witco Chemical Co., USA)(the major component is $K_2Cr_2O_7$) in 1 L deionized water] at 25 ℃ for 3 to 6 min and washed with deionized water 3 min for aluminum AA 1100 and aluminum alloy AA 6061, 5 min for AA 2024 and AA 7075, and 6 min for AA 2014, respectively. After air-dried, the chromated specimens were wrapped with Kimwipes and stored in a dessicator at 25 ℃.

Inhibition test

Potassium dichromate salt was dissolved and diluted with deionized water to 2,000 to 8,000 mg kg^{-1}. The inhibitory activity was measured by the paper disk method[9] (diameter 8 mm, Toyo Seisakusho Co., LTD, Japan). Fifty μ L of chromate solution was added to the paper disk, put on potato dextrose agar with 1 mL spore suspension of test organism (about 10^7 spores mL^{-1}), and incubated at 37 ℃ for 1 to 5 days. The antimicrobial activity was calculated from the clear zone of a standard curve of authentic chromate or counted the viable colony with pour plate method.

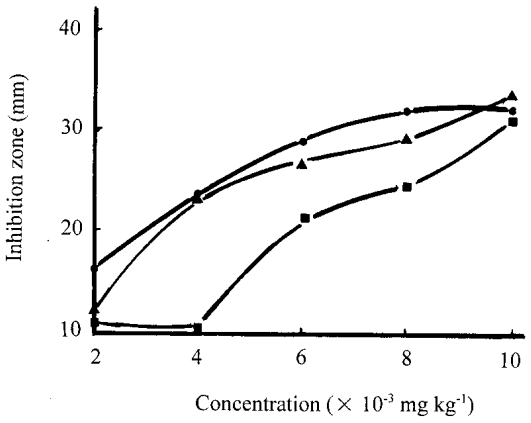

圖 1 鉻酸鹽對供試菌株抑制作用

Fig. 1 Inhibitory activity of chromate on test organisms.

●---● *Aspergillus versicolor*

■---■ *Penicillium funiculosum*

▲---▲ *Cladosporium resinae*

Corrosion test

According to the MIL-STD-810D Test Method[6], spore suspension of test organism 1 mL (about 10^7 spores mL^{-1}) was inoculated on the surface of aluminum alloy. After drying aluminum alloy was put in the sealed dessicator with different water activities at 25 ℃ for 28 days or 3 months. Microbial corrosion was observed under light (Nikon SMZ-U, Japan) and scanning electron microscopes (Hitachi Model S-550, Japan) at 15 to 20KV, then washed the surface with deionized water and observed the surface of aluminum alloy again.

Energy dispersive spectrometer (EDS)

Composition of aluminum alloy was *analyzed* by energy dispersive spectrometer (Kevex level IV)[10]. After drying, the specimen were fixed on specimen stub by electroconductive tape, and observed under scanning electron microscope at 15 to 20 KV. Microbial corrosion of aluminum alloy was also compared between corrosion site and control area with the microbial growth and element analysis.

RESULTS

Effect of chromate on the growth of test organisms

表 2　供試菌株在鋁合金上生長 3 個月之情形

Table 2　Growth of test organisms on aluminum alloys for 3 months

Aluminum alloy 鋁合金 / Test organism 供試菌株	AA 1100				AA 2014				AA 2024				AA 6061				AA 7075			
	Blank 對照組		Chromate 鉻酸鹽轉化		Blank 對照組		Chromate 鉻酸鹽轉化		Blank 對照組		Chromate 鉻酸鹽轉化		Blank 對照組		Chromate 鉻酸鹽轉化		Blank 對照組		Chromate 鉻酸鹽轉化	
	0.84 *	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90	0.84	0.90
Asperillus flavus	+++	++++	++	+++	+++	+++	++	+++	++	+++	++	+++	+++	+++	++	++	-	-	+++	+++
Aspergillus niger	++	++	++	++	++	+++	++	+++	+++	+++	+++	+++	+++	+++	++	+++	-	-	+	+++
Aspergillus versicolor	+++	+++	+	++	++	+++	-	-	+	+++	-	+	+	+	-	-	-	-	+	+
Chaetomium globosum	+++	++++	+	+++	++	++	-	++	++	+++	-	+++	++	+++	+	++	-	-	+	++
Penicillium funiculosum	+++	++++	+	++	+++	++++	+	+++	+++	+++	++	++	+++	+++ +	+	++	-	-	++	+++
Cladosporium resinae	+	++	+	++	-	-	-	-	-	++	-	++	-	+	-	+	-	-	-	++
Penicillium sp. AM-F5	++	+++	+	++	+	++	-	+	+	+	-	+	+	+	-	+	-	-	-	++

* : Aw was 0.842 and 0.901, respectively
\- : No growth
\+ : Slight growth
++ : Moderate growth
+++ : Heavy growth
++++ : Abound growth
Blank : Aluminum alloy without chromate treatment
Chromate : Aluminum alloy with chromate conversion coating

* ：水活性分別爲0.842和0.901
\- ：未生長
\+ ：微量生長
++ ：中等程度生長
+++ ：生長良好
++++ ：生長茂密
對照組 ：鋁合金未用鉻酸鹽轉化處理
鉻酸鹽轉化：鋁合金以鉻酸鹽轉化塗敷

The inhibitory zone of test microbes increased with the concentration of chromate (Fig. 1). The growth of *A. ersicolor* and *Clad. resinae* with 3.0-3.5 × 10^7 spores per mL was inhibited at 8,000 mg kg^{-1} chromate when it was added at zero time. While the growth of *P. funiculosum* with 2.5 × 10^7 spores per mL was inhibited at 8,000 mg kg^{-1} chromate at the second day. The inhibitory activity of chromate on the growth of *P. funiculosum* was lower than those of *A. versicolor* and *Clad. resinae.*

Growth of test organisms on the surface of aluminum alloy

The growth of test organisms on the surface of chromate conversion coating aluminum alloy at 25 ℃ for 3 months is shown in Table 2. The microbial growth at Aw 0.901 was heavier than those at Aw 0.842. Chromate conversion coating inhibited the growth of *A. versicolor* and *P. funiculosum.* Microbial growth on the surface of chromate conversion coating aluminum AA 1100 and aluminum alloy AA 6061 was less than the control, whereas the inhibitory phenomena of chromate conversion coating were not significant in aluminum alloys AA 2014, AA 2024, and AA 7075.

Corrosion of aluminum alloy

Microbial corrosion of aluminum alloy with chromate conversion coating is presented in Figs. 2 to 5. For 3 months incubation, aluminum alloy with chromate conversion coating had higher resistance to the microbial corrosion than the control. All the aluminum alloys without chromate conversion coating had microbial corrosion on the surface, and the degree of microbial corrosion depended on the test alloys and test microbes. Aluminum alloy AA 7075 had very serious corrosion on the surface for 5 days incubation, whereas aluminum AA 1100 and aluminum alloy AA 6061 had less corrosion.

P. funiculosum had heavy growth with lots of spores on the surface of aluminum AA 1100 and aluminum alloy AA 6061, and the corrosion was extended from the central part to the exterior area (Fig. 2). However, the growth of *Clad. resinae* was moderate with some spores presence, and a biofilm was formed on the surface of aluminum alloy (Fig. 3). Therefore, the corrosion of *P. funiculosum* and *Clad. resinae* on aluminum alloy was very serious. Although, the growth of *A. flavus, A. niger, A. versicolor, Chaet. globosum,* and *Penicillium* sp. AM-F5 were moderate on the surface of aluminum alloy, however the corrosion of these microbes was not so significant as those of *P. funiculosum* and *Clad. resinse.*

Microbes grew and formed a biofilm on the surface of aluminum alloys AA 2014 and AA 2024. *P. funiculosum, Clad. resinae,* and *Penicillium* sp. AM-F5 had localized corrosion on the surface and some mycelia adhered tightly in the corrosion site. *A. versicolor* had pitting on the surface when the mycelia were removed from the surface of aluminum alloy. Since the corrosion area was very consistent with the biofilm formation, mycelia adhered on the surface would enhance the microbial corrosion of aluminum alloy (Fig. 4).

Microbial corrosion of aluminum alloy AA 7075 was found from the mycelial growth area to the exterior area (Fig. 5). Therefore, the microbial metabolites were very important in the corrosion. Chromate conversion coating of aluminum alloy will retard the microbial growth and reduce the microbial corrosion. Coating method also plays an important role in the prevention of microbial growth and corrosion. Uneven coating and small hole presence on the surface will accumulate the contaminated substances and stimulate the microbial growth and corrosion. *P. funiculosum* was the most potential organism in corrosion of aluminum alloy.

Metallic ion and microbial growth

Aluminum alloy AA 7075 contains 2.1 to 2.9% magnesium to enhance the hardness of alloy, and has the most serious microbial corrosion among the 5 test alloys. The ratio of metal content in corrosion site with test organisms for 3 months to control area of aluminum alloy AA 7075 is indicated in Table 3. The ratio of magnesium content in corrosion site to control area decreased 59% in *P. funiculosum,* and 15% in *A. versicolor*, whereas the ratioes of copper and zinc contents increased 3 to 103%. The decrease of magnesium content in corrosion site might be due to the formation of magnesium oxide or the uptake of magnesium ion by the test organisms during incubation. Microbial growth in aluminum alloy AA 7075 was poor and some mycelia were leaked from the surface of aluminum alloy, but these phenomena were

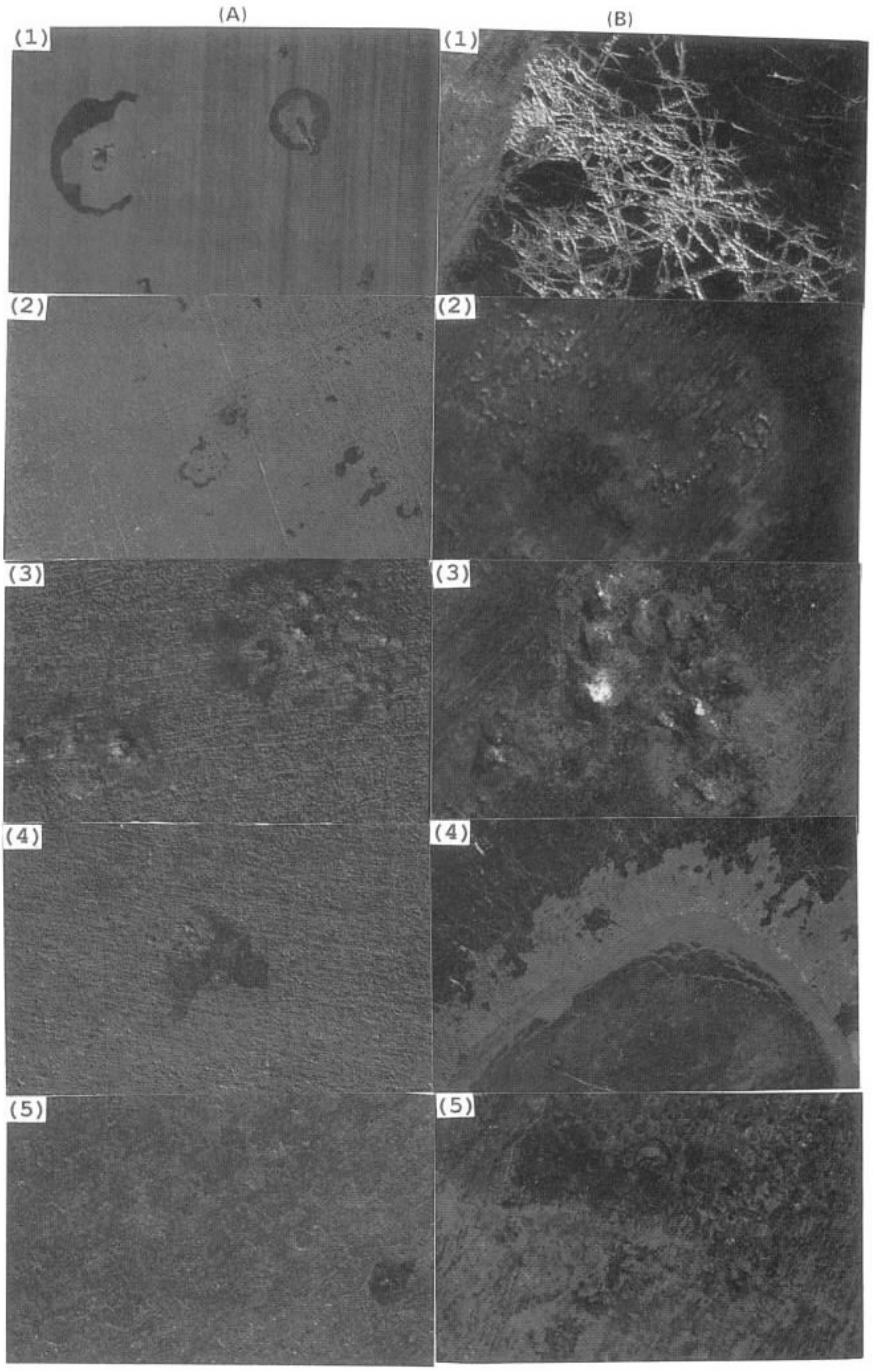

圖 2　*Penicillium funiculosum* 對鋁合金之腐蝕情形(× 15)

Fig. 2　Microbial corrosion of aluminum alloys by *Penicillium funiculosum* (× 15)

(A)鉻酸鹽轉化塗敷鋁合金
　With chromate conversion coating
(B)未經鉻酸鹽轉化塗敷鋁合金
　Without coating
(1)AA 1100　　(4)AA 6061
(2)AA 2014　　(5)AA 7075
(3)AA 2024

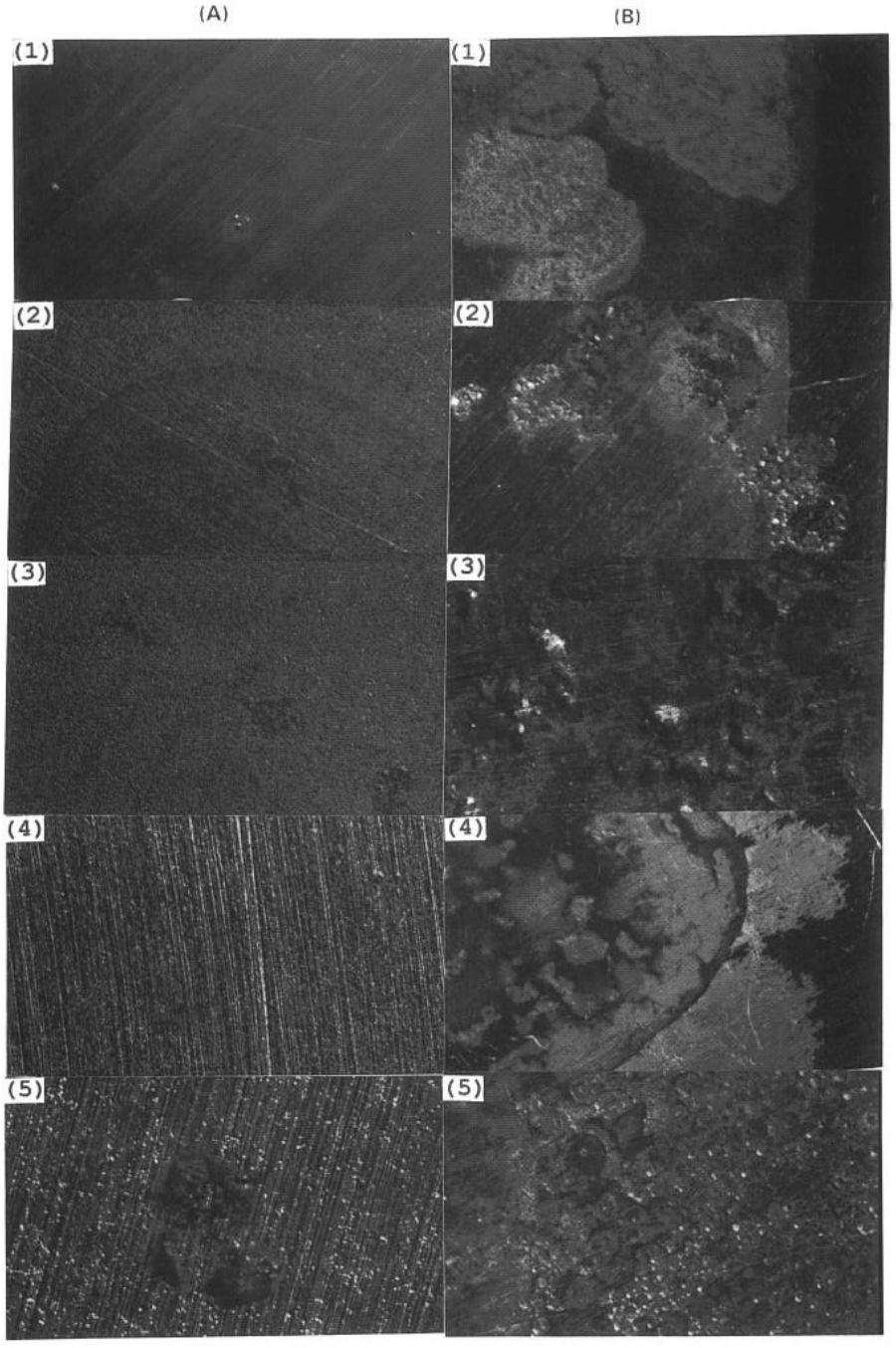

圖 3　*Cladosporium resinae* 對鋁合金之腐蝕情形(× 15)

Fig. 3　Microbial corrosion of aluminum alloys by *Cladosporium resinae* (× 15)

(A)鉻酸鹽轉化塗敷鋁合金
With chromate conversion coating

(B)未經鉻酸鹽轉化塗敷鋁合金
Without coating

(1)AA 1100　　(4)AA 6061

(2)AA 2014　　(5)AA 7075

(3)AA 2024

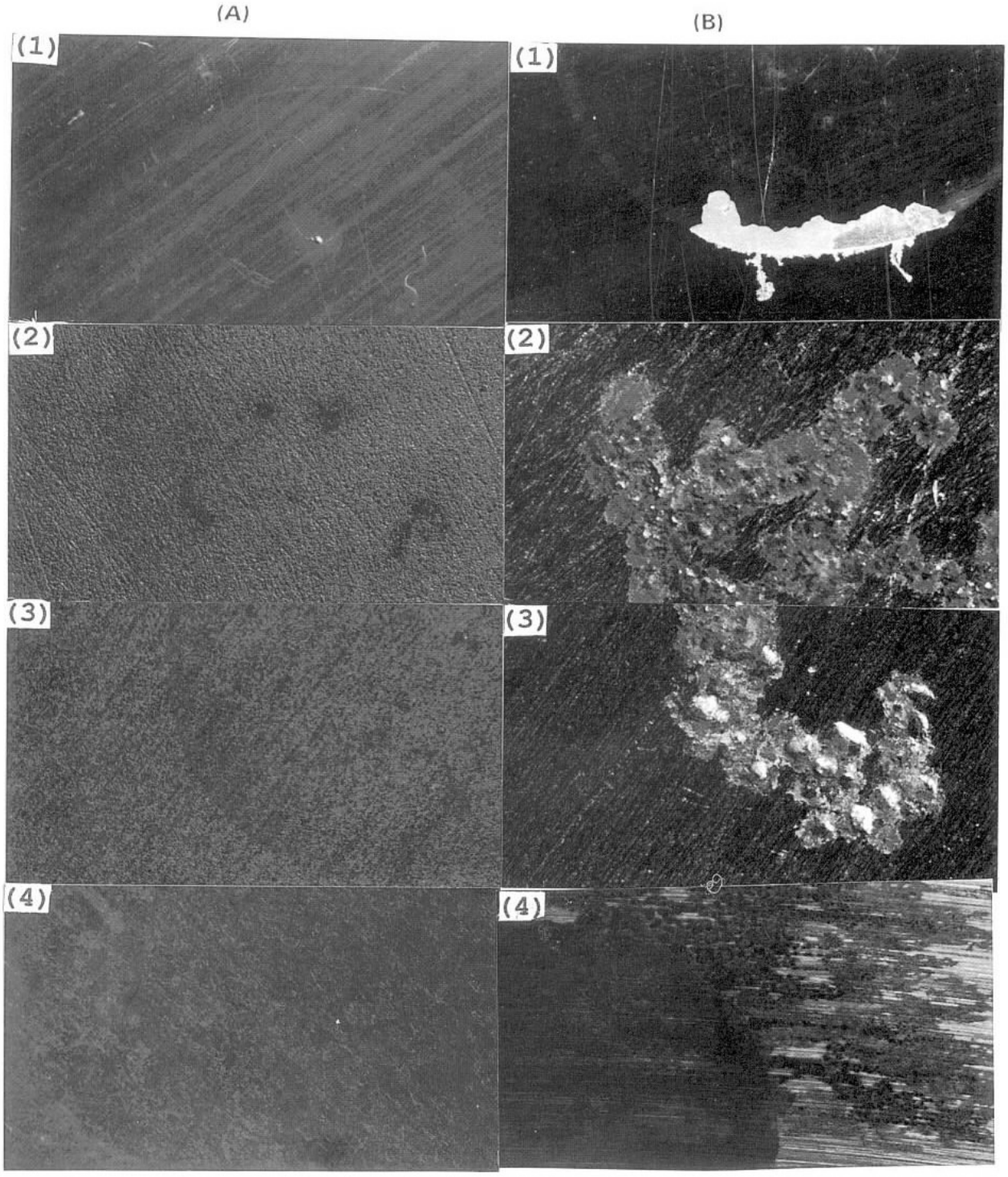

圖 4　*Penicillium* sp. AM-F5 對鋁合金之腐蝕情形(× 15)

Fig. 4　Microbial corrosion of aluminum alloys by *Penicillium* sp. AM-F5 (× 15)

(A)鉻酸鹽轉化塗敷鋁合金

With chromate conversion coating

(B)未經鉻酸鹽轉化塗敷鋁合金

Without coating

(1)AA 1100　　(3)AA 2024

(2)AA 2014　　(4)AA 7075

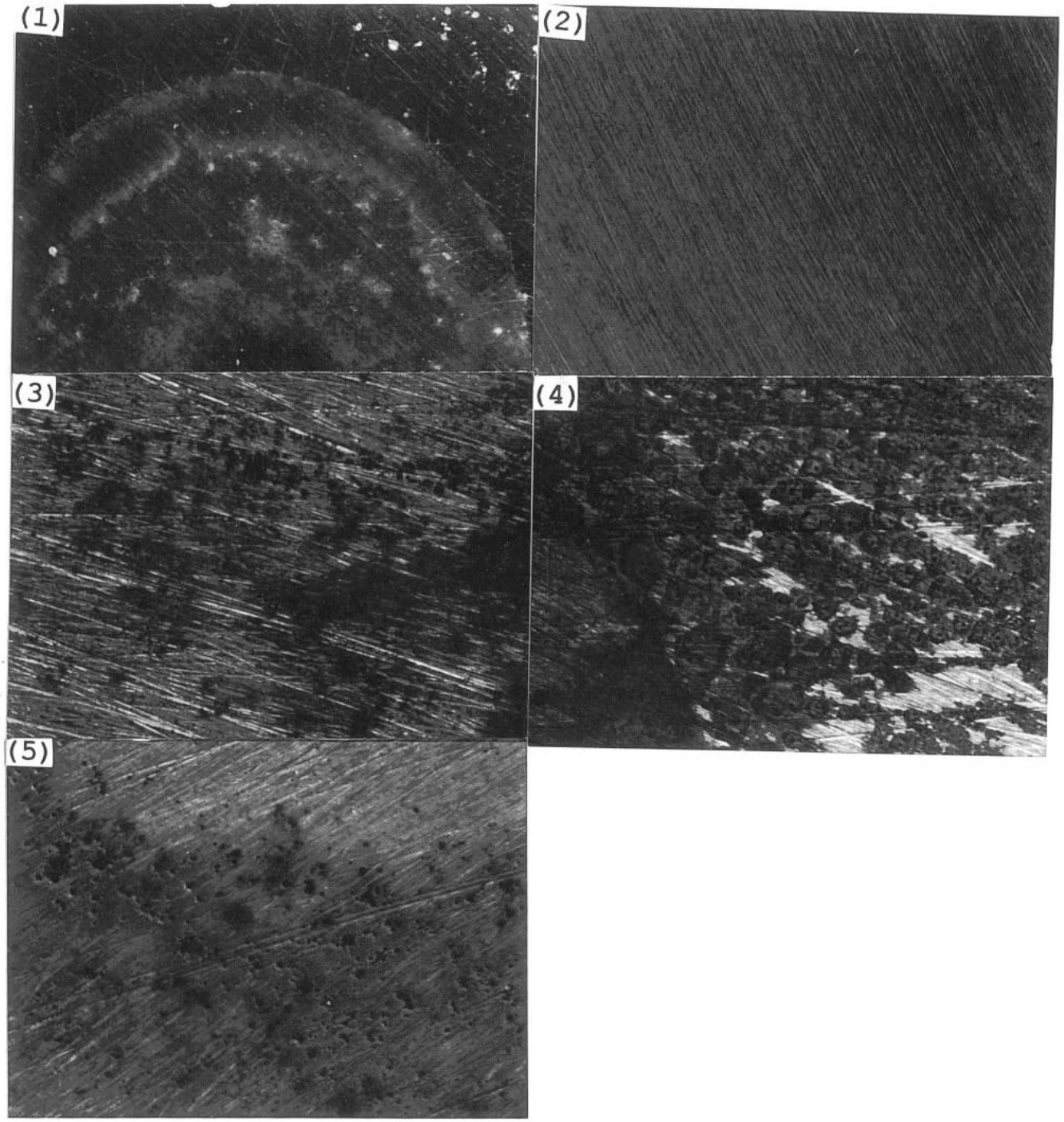

圖 5　*Aspergillus versicolor* 對鋁合金之腐蝕情形(× 15)

Fig. 5　Microbial corrosion of aluminum alloys by *Aspergillus versicolor* (× 15)

(1)AA 1100　　(4)AA 6061

(2)AA 2014　　(5)AA 7075

(3)AA 2024

表 3　鋁合金 AA7075 在腐蝕區及未腐蝕區之元素重量比例

Table 3　Ratio of element weight between corrosion site to control area of aluminum alloy AA 7075

Element 元素 / Test organism 供試菌株	Cu 銅	Mg 鎂	Zn 鋅
Aspergillus versicolor	1.64	0.85	1.62
Chaetomium globosum	1.03	0.63	1.17
Penicillium funiculosum	1.05	0.41	2.03
Cladosporium resinae	1.32	0.72	1.03
Penicillium sp. AM-F5	1.10	0.62	1.20

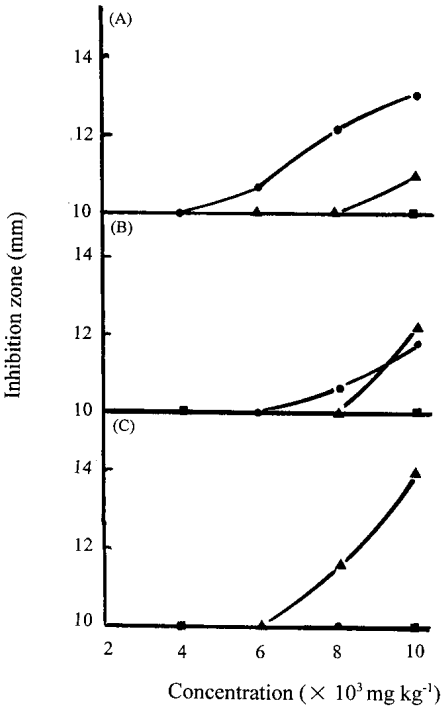

圖 6　金屬離子對供試菌株之抑制作用

Fig. 6　Inhibitory activity of metallic ion on test organisms.

(A) *Aspergillus versicolor*

(B) *Penicillium funiculosum*

(C) *Cladosporium resinae*

■---■ $MgSO_4 \cdot 7H_2O$

●---● $ZnSO_4 \cdot 7H_2O$

▲---▲ $CuSO_4 \cdot 7H_2O$

not found in other alloys. Aluminum alloy AA 7075 contains 5.1 to 6.1% zinc and the value was the highest one among the 5 test alloys. Zinc might be solubilized by the acid secretion of test organisms during incubation, and inhibited the microbial growth. Therefore, microbial growth on the surface of aluminum alloy AA 7075 without chromate conversion coating was less than that of chromate conversion treatment.

The inhibitory zone of *A. versicolor*, *P. funiculosum*, and *Clad. resinae* increased with the concentration of $ZnSO_4.7H_2O$ and $CuSO_4.7H_2O$, while the inhibitory activity of $MgSO_4.7H_2O$ was negligible at 10 g L^{-1} (Fig. 6). *A. versicolor* was the most sensitive strain to the presence of sulfate solution, while *P. funiculosum* was the least one. The inhibitory activity of copper ion was higher than that of zinc ion in *A. versicolor* and *P. funiculosum*.

Elemental analysis of energy dispersive spectrometer

Microbial corrosion of the aluminum alloy was observed under light and scanning electron microscopes. Localized corrosion was found beneath the microbial colony, and the intergranular corrosion was the major type of localized corrosion (Figs. 7 and 8). From the energy dispersive spectrometer of elemental analysis, it was found that the element contents of alloy had significant difference between corrosion site and control area. Oxygen, phosphorus, chlorine, sulfur, potassium, and sodium were found in the corrosion site, whereas these elements were absent in the control area. Copper, manganese, iron, silicon, and zinc contents increased in corrosion area, while magnesium content decreased (Fig. 9).