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Corrosion Behavior of Aluminum Alloys in Seawater

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Corrosion results of aluminum alloys exposed to seawater at Xiaomai Island, Qingdao, China for 16 years were obtained. Corrosion behavior of aluminum alloys in seawater was discussed. LF2Y2, LF6M with and without Al-cold, 180YS and LF21M had a good corrosion resistance in seawater. Seawater corrosion resistance of LY12CZ without Al-cold and LC4CS without Al-cold were very poor. Al-clad layer of LY12CZ and LC4CS played a sacrificial anode role in corrosion process, and their base alloys were protected. Fouling organism could cause localized corrosion of aluminum alloys. Effect of fouling on corrosion of aluminum alloys in seawater was obvious. Mg, Mn can improve the corrosion resistance of aluminum in seawater. Si obviously deteriorates its corrosion resistance. Cu seriously deteriorates its corrosion resistance.

Keywords *: seawater corrosion, aluminium alloy, exposure test, fouling, alloy element*

1. Introduction

Aluminum alloys with higher strength, good performance of machining and seawater corrosion resistance have been widely used in seawater. Corrosion failures by local attack such as by pitting, crevice corrosion or exfoliation, or stress cracking are characteristic of many aluminum alloys exposed to seawater. Difference of corrosion resistance of aluminum alloys containing various alloying elements, or exposed to seawater at various sea areas was serious.[1-3] Hence, it's essential to accumulate the corrosion data of aluminum alloys in seawater at various sea areas and to study their corrosion behavior and rule in order to apply rationally and successfully.

Under the financial support of National Nature Science Fund of China, long-term corrosion tests of aluminum alloys in Qingdao Sea area of China have exploited. In this article, corrosion data of aluminum alloys in seawater for 16 years are reported. Their corrosion behavior is discussed.

2. Experimental

There are 12 types of aluminum alloys tested, chemical components of which are listed in Table 1. These aluminum alloys came from batch products of North-east Light Alloy Machining Factory, prepared by Beijing Non-ferrous Metals Research Institute. The size of samples is 200mm × 100mm × (2~6)mm. Every material in each measurement period has three parallel samples.

Surface treatment of the samples was done before exposure. The process following: rinsed by gasoline → washed by metal abluent → rinsed by water → immersed in 10% NaOH for 4 min → rinsed by water → immersed in 30% HNO_3 for 2 min → rinsed by water → dehydrated in anhydrous alcohol → dry → standby. The carbon-deposit samples were put into the solution of 52% dichloromethane + 26.45% mixed cresol + 4.9%methylbenzene + 16.65% mollin for 12 hours to remove carbon and then swabbed by alcohol.

The experiments were performed at Xiaomai Island, Qingdao, China, viz. 36° 03′ N, 120° 25′ E. The mean tem-

Table 1. Chemical composition of aluminum alloys tested1, mass %

Alloys	Cu	Mg	Mn	Si	Fe	Zn	Cr	Ti	Be
L4M	0.013			0.16	0.23				
LF2Y2	0.009	2.03	0.42	0.15	0.27				
LF3M	0.006	3.86	0.40	1.25	0.18				
180YS	<0.1	5.46	0.57	0.12	0.18		0.13	0.07	
LF6M(BL)2	<0.1	6.44	0.64	0.12	0.21			0.096	0.0012
LF6M(QL)3	<0.1	6.44	0.64	0.12	0.21			0.096	0.0012
LF21M	<0.1		1.00	0.18	0.55				
LD2CS	0.26	0.87	0.18	0.89	0.27	0.20			
LY12CZ(BL)2	4.59	1.48	0.59	0.12	0.23	<0.2		<0.05	
LC4CS(BL)2	1.49	2.30	0.27	0.13	0.36	5.89	0.13	<0.05	
LY12CZ(QL)3	4.59	1.48	0.59	0.12	0.23	<0.2		<0.05	
LC4CS(QL)3	1.49	2.30	0.27	0.13	0.36	5.89	0.13	<0.05	

Note : 1 Al is remainder. 2 With Al-clad. 3 Al-clad of the samples surface was taken out by washing with NaOH solution.

perature of seawater is 13.7℃, maximum 27℃, minimum -1℃, salinity is about 32, and pH is around 8.2. The mean flowing rate of seawater is less than 0.1m/s.

The samples were exposed in fixed full immersion mode. And the samples were immersed 0.5 to1.2m under mean low water level. Exposure times were 1, 2, 4, 8 and 16 years. Exposure test and the treatment of samples before and after exposure accord with GB5776-86.

3. Results and discussion

3.1 Pitting

Pitting is common type of aluminum alloys in seawater. Maximum pitting depths of that are given in Fig. 1. Maximum pitting depth of pure aluminum L4M exposed to seawater for 2 years is 0.40mm, and that of L4M exposed for 16 years is 1.47mm.

Al-Mg alloys LF2Y2, LF6M(BL), LF6M(QL) and 180YS as well as Al-Mn alloy F21M were good pitting resistance in seawater. Exposing 2 years, no pit depth of that could be measured was found at the surface. For exposure 8 years, their pitting depths was less than 0.40mm, and for exposure 16 years, pitting depths are less than 0.9 mm. Galvanic corrosion did not take place between Al-clad of LF6M(BL) and basic alloy. Pitting resistance of Al-Mg-Si alloys LF3M is poorer than that of LF2Y2, LF6M(QL), F6M(BL), 180YS and LF21M. Maximum pitting depth of LF3M for exposure 1 year in seawater is 0.40mm, and 16 years 1.74mm.

Seawater corrosion resistance of Al-Cu-Mg-Si alloy LD2CS is poor. Exposing 1year, its maximum pitting depth is 0.85mm. For exposure 16 years, LD2CS sample thickness of which is 2.1mm has been corroded perforation.

Corrosion of Al-Cu-Mg alloy LY12CZ(QL) and Al-Zn-Cu-Mg alloy LC4CS(QL) in seawater were very serious. Maximum pitting depths of they were 2.30 and 1.36mm for exposure 1 year, and that were 2.65 and 2.06mm for exposure 16 years. In addition, flanks of LY12CZ(QL) and LC4CS(QL) samples occurred seriously stress corrosion cracking. Their exposure test was done only for 2 years.

Basic alloy of LY12CZ(BL) and LC4CS(BL) was protected because Al-clad of the sample surface play a sacrifice anode part. Exposing to seawater from 1 to 8 years, maximum pitting depths of LY12CZ(BL) and LC4CS(BL) had little change, and their pitting depth were less than 0.25 and 0.10mm. For exposure 16 years, pitting depth of LY12CZ(BL) and LC4CS(BL)increased obviously, maximum pitting depth were 0.55 and 0.45mm.

Aluminum alloys exposed to seawater were fouled by marine organisms such as ostrea, encrusing bryozoa, hydroide and marine algaes. Corrosion production affects the organism fouling. For Aluminum alloys corrosion area of that is more such as LD2CS, LC4CS(BL) and LY12CZ (BL), fouling area is less. Fouling area of LD2CS, LC4CS(BL) and LY12CZ(BL) for 2~16 years exposure were 20~40%. Fouling area of other aluminum alloys were 50~80%. Deeper pits on aluminum alloys surface occurred all at underside of ostrea and hydroide. Fouling organisms can cause localized corrosion of aluminum alloys. It is shown effect of fouling on corrosion of aluminum alloys was obvious.

3.2 Crevice corrosion

Aluminum alloys tend to crevice corrosion in seawater. Maximum crevice corrosion depths of aluminum alloys are given in Fig. 2. LF2Y2, LF6M(BL), LF6M(QL) and

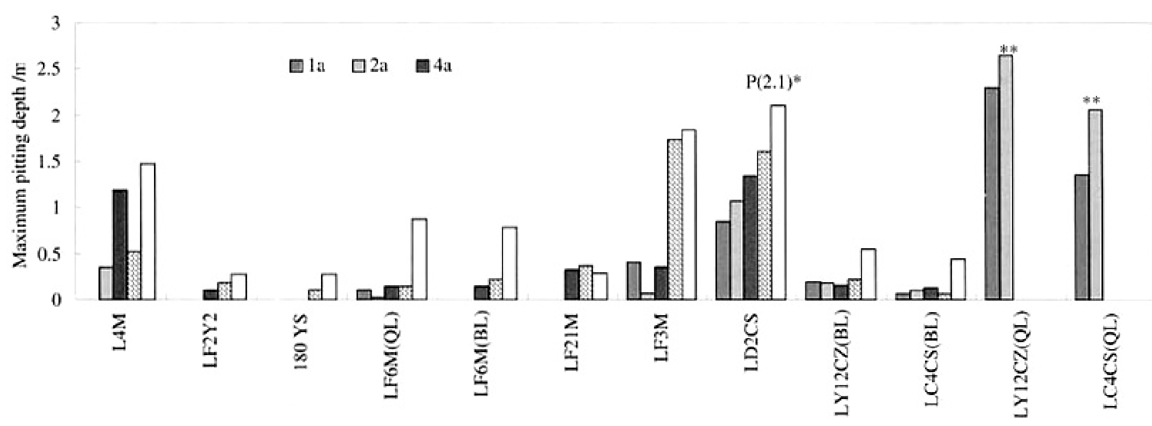

Fig. 1. Maximum pitting depth of aluminum alloys in seawater
* P=Perforation, the thickness of samples is 2.1mm
**Exposure test of LY12CZ(QL) and LC4CS(QL) was done only for 2 years.

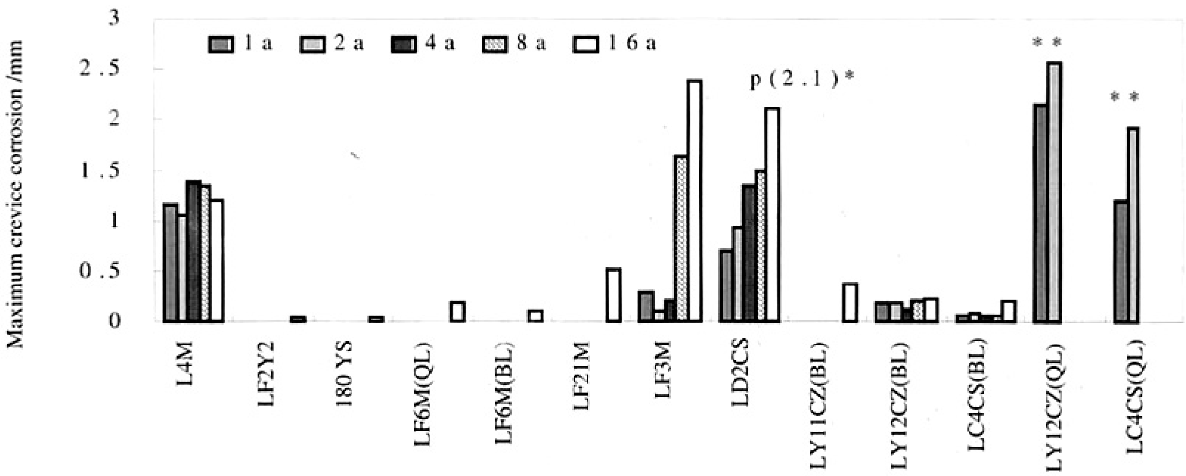

Fig. 2. Maximum crevice corrosion depths of aluminum alloys in seawater
* P=Perforation, the thickness of samples is 2.1mm°
**exposure test of LY12CZ(QL)and LC4CS(QL) was done only for 2 years

180YS as well as LF21M showed a good resistance to crevice corrosion in seawater. Maximum crevice corrosion depths of LF2Y2, LF6M(BL), LF6M(QL) and 180YS in seawater for 16 years were less than 0.2mm, and one of LF21M was 0.52mm. L4M and LD2CS have poorer resistance to crevice corrosion. Maximum crevice corrosion depths of L4M and LD2CS for 1 year were1.15 and 0.70mm, and for 16 years, LD2CS had been corroded perforation. Crevice corrosion resistance of LY12CZ(QL) and LC4CS(QL) is very poor, maximum crevice corrosion depths of that in seawater for 1 year were 2.16 and 1.20mm.

Al-clad of LY12CZ(BL) and LC4CS(BL) have protection effect for crevice corrosion of basic alloy. Exposing to seawater from 1 to 16 years, crevice corrosion depths change of LY12CZ(BL) and LC4CS(BL) was less, and their crevice corrosion depths were less than 0.25 and 0.10mm.

The result of Fig. 1 and Fig. 2 showed that crevice corrosion behavior of aluminum alloys in seawater are similar to the pitting behavior. Aluminum alloys that have a relatively high resistance to pitting in seawater also reveal a relatively high resistance to crevice corrosion, and vice versa.

3.3 Corrosion rate

Average corrosion depth vs. exposure time curves of typical aluminum alloys exposed to seawater is given Fig. 3. Exposing first year, Corrosion rates of aluminum alloys were higher. Corrosion rate slobbered after exposure 1 year. Corrosion rate of LD2CS and LC4CS(BL) after exposure 8 years appeared a increscent trend.

Corrosion rate of aluminum alloys tested in seawater

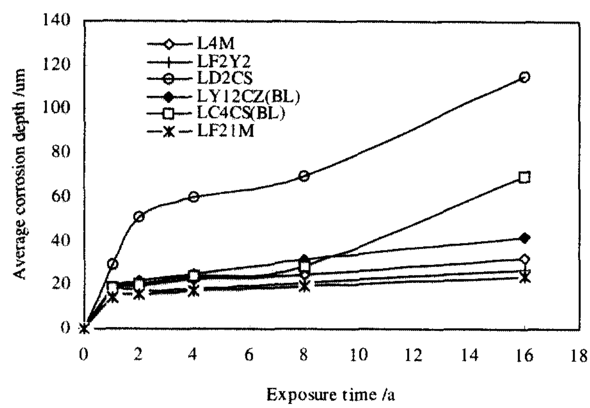

Fig. 3. Average corrosion depth - exposure time curves of alumimum alloys in seawater

Table 2. Corrosion rates of aluminum alloys in seawater

Alloys	Exposure time, a				
	1	2	4	8	16
L4M	18	9.9	5.7	2.7	2.0
LF2Y2	17	8.7	4.5	2.5	1.7
180 YS	15	8.4	4.4	2.5	1.6
LF6M(QL)	13	9.3	5.6	3.0	1.9
LF6M(BL)	14	8.0	4.5	2.5	1.8
LF21M	14	7.8	4.3	2.4	1.5
LF3M	16	8.5	4.6	3.5	2.6
LD2CS	29	25	15	8.7	7.2
LY12CZ(QL)	220	120	-1	-	-
LC4CS(QL)	170	99	-1	-	-
LY12CZ(BL)	18	12	6.2	4.4	2.6
LC4CS(BL)	19	10	5.9	3.6	4.4

Note: 1. The exposure test was done for 2 years only.

is listed in Table 2. Corrosion rates of LF2Y2, LF6M(BL), LF6M(QL), 180YS and F21M in seawater were lower. Their corrosion rates were between 13 and 17μm/a for exposure 1 year, and ones were between 1.5 and 1.9μm/a for exposure 16 years. Corrosion rates of L4M exposed to seawater for 1 year and 16 years were 18 and 2.0μm/a. Corrosion rate of LY12CZ(QL)and LC4CS(QL) were vary high, and were about 10 times as high as one of L4M. Magnitude of corrosion rate of aluminum alloy in seawater reflected degree of itself localized corrosion.

Exposing from 1 to 8 years in seawater, corrosion rate of LC4CS(BL) was closed to that of L4M. Exposing 16 years, corrosion rate of LC4CS(BL) increased, and is 4.4μ m/a. Thickness of Al-cad layer of LC4CS(BL) is about 60μm. Average corrosion depth of LC4CS(BL) for exposure 16 years was about 70μm. Al-clad layer of LC4CS(BL) had been corroded out. Corrosion rate of LC4CS(BL) had increased without protection effect of Al-clad layer. Continuing exposure, it will occur serious corrosion.

Corrosion rate of LY12CZ(BL) exposed to seawater for 16 years was 2.6μm/a. Thickness of Al-clad layer of LY12CZ(BL) is about 150(m. Average corrosion depth of LY12CZ(BL) for exposure 16 year was about 40μm. Al-clad layer of LY12CZ(BL) still possess protection effect.

Corrosion rates means decreasing uniformly thickness. However, corrosion failures of aluminum alloys in seawater are arisen from local attack such as pitting, crevice corrosion or exfoliation, or stress corrosion cracking. For appraising seawater corrosion resistance of aluminum alloy, practicality of the corrosion rate is very less. Misconstruction is arisen easily looking at corrosion rate only.

3.4 Effect of alloy elements on corrosion resistance of aluminum in seawater

Seawater corrosion resistance of LF2Y2, LF6M(BL), LF6M(QL), 180YS and LF21M is better than that of L4M. It is shown that Mg and Mn can enhance corrosion resistance of aluminum in seawater. Of aluminum alloys, Al-Mg alloys and Al-Mn alloys have the best resistance to corrosion in seawater.

Of adding elements of aluminum alloys, Cu has the best aggrandizement effect, but damage of Cu on corrosion resistance of aluminum is also most. Cu is a very strong cathodic phase composition. In corrosion process, it has remarkable second separating out. This second separating out shall quicken up corrosion of aluminum. Corrosion of aluminum alloys containing a higher Cu in seawater is serious without Al-clad or other protection means.

Literature considering, effect of Si on corrosion resistance of aluminum is less.[4),5)] However, exposure result of this article shown that Si obviously deteriorates resistance to pitting for aluminum in seawater. Compare LF3M with LF2Y2, LF6M(BL), 180YS and LF21M, Si content of LF3M is higher, as high as 1.25%. Si in LF3M is added for alloy element, however Si in LF2Y2, LF6M(BL), 180YS and LF21M are impurity, less than 0.4%. LF3M had a poorer resistance to pitting in seawater than did LF2Y2, LF6M(BL), 180YS and LF21M. LD2CS showed a poor seawater corrosion resistance, Cu and Si content in which are 0.27% and 0.89%.

4. Conclusions

1) LF2Y2, LF6M with and without Al-cold, 180YS and LF21M had a good corrosion resistance in seawater. Seawater corrosion resistance of LY12CZ without Al-cold and LC4CS without Al-cold were very poor.

2) Al-clad layer of LY12CZ and LC4CS played a sacrificial anode role in corrosion process, and their base alloys were protected.

3) Fouling organism could cause localized corrosion of aluminum alloys. Effect of fouling on corrosion of aluminium alloys in seawater was obvious.

4) Mg, Mn can improve the corrosion resistance of aluminum in seawater. Si obviously deteriorates its corrosion resistance. Cu seriously deteriorates its corrosion resistance.

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