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Atmospheric Corrosion of 7B04 Aluminum Alloy in Marine Environments

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Outdoor exposure tests using of 7B04 aluminium alloy samples including plate, tensile and various SCC samples were carried out in Tuandao station, Shandong province (East of China) and Wanning station, Hainan province (South of China). Corrosion characteristics including weight loss, microstructure, tensile strength and SCC susceptibility were investigated. The corrosion rates in Tuandao and Wanning showed high to low and the corrosion rates changed to the following equation of $w=at^b$ ($b<1$). The corrosion of 7B04 aluminium alloy in Wanning was more serious than that in Tuandao. Pitting appeared at early stage of expose test, and it can be changed to general corrosion with test time extension. The 7B04 aluminium alloy of which specimen shapes are forging and thick plate also showed SCC (Stress corrosion cracking) in the marine atmosphere. The higher SCC sensitivity was observed in Wanning station than in Tuandao station. The 7B04 aluminium alloy with a high stress level was more sensitive to SCC. Intergranular and transgranular or a mixed mode of cracking can be observed in different marine exposure.

Keywords: *7B04 aluminum alloy, atmospheric corrosion, SCC*

1. Introduction

The performance of airplane is improving with the research and application of advanced high strength materials. China has complicated geography and marine climates. The damage of structure materials and airplane are mainly corrosion in service environments with difference of climates and service life [1]. Corrosion is not only decrease the structure strength of airplane, but also effect the structure integrity, even endanger airplane's safety or leading to accident. The research on corrosion of high strength materials in different environments is related to design of structure and selection of materials. It is also important to improve adaptability of climates and airplane safety. There have been some field exposure studies that investigate the atmospheric corrosion of aluminum alloys in various environments [2-8]. The results showed that pitting corrosion [5-8], intergranular corrosion [3,5,6,8], and exfoliation corrosion [1-5] occur in the tropical marine atmosphere. Both pitting and intergranular corrosion occur at the early stage of corrosion in a coastal environment [5], exfoliation corrosion initiates from hydrogen-assisted intergranular cracks, and then propagates and broadens extensively due to the wedge effect of the corrosion products generated along the grain boundaries [6].

7B04 is Al-Zn-Mg-Cu type of aluminium alloy with advantage of high strength and low density. It is widely used to manufacture airplane structures in many airplanes [9]. However, only a few studies have been reported on corrosion behaviour of 7B04 aluminium alloy [10-12], the relationship between the weight loss or corrosion rate and the microstructure or the further corrosion process has not been established. In this work, corrosion behavior of 7B04 aluminum alloy exposed in a tropical marine atmosphere for 5 years was investigated. The corrosion behaviour, failure analysis and SCC of 7B04 aluminium alloy in marine coast were studied in this article.

2. Experimental Procedures

2.1 Material and samples

The chemical compositions and mechanical properties of 7B04 aluminium alloy were listed in Table 1 and Table 2 respectively. The size of plate specimens used for atmospheric exposure is 50 mm × 100 mm × (3～5) mm. The C-ring specimens take from the forging and thick plates in S-L direction according to ASTM G38. Pre-cracked SCC specimens take from the 40mm thick plate in S-L direction according to ASTM G168. The first letter, S is the direction of applied stress, means short-transverse.

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Table 1 The chemical compositions of 7B04 alloy (mass fraction, %)

Al	Zn	Cu	Mg	Mn	Cr	Fe	Ti	Ni	Si	Others
Bal	5.0-6.5	1.4-2.0	1.8-2.8	0.2-0.6	0.1-0.25	0.05-0.25	≤ 0.05	≤ 0.1	≤ 0.1	0.1

Table 2 Mechanical properties of 7B04 alloy

identity	Sample direction	tensile strength/MPa	yield strength/MPa	sectional contraction/%
40mm plate, T741	S-L	507	437	9.5
50mm plate, T7451	L-T	511	445	10.0
55mm plate, T651	L-T	520	440	5.0

Table 3 Environmental parameters in Tuandao and Wanning station

Parameter	Wanning	Tuandao
Average temperature (℃)	24.2	12.3
Average relative humidity (%)	86	71
Time-of-wetness (h/a)	6020	4049
Precipitation of rain (mm/a)	1515	562
Dew time (d/a)	148	51
Sun shine (h/a)	2026	2161
Cl^- deposition ($mg/100cm^2 \cdot d$)	0.128	0.138
Cl^-concentration in air ($mg/\cdot m^3$)	0.037	0.151
SO_2 deposition ($mg/100cm^2 \cdot d$)	---	1.181
SO_2 concentration ($mg/\cdot m^3$)	0.092	0.340
NO_2 concentration in air ($mg/\cdot m^3$)	0.003	0.002
pH of rain	5.1	7.1

Table 4 Mass loss-time regression result of outdoor exposure tests

Outdoor exposure test site	Regression equation and correlation coefficient
Tuandao station	$w = 6.7284t^{0.6252}$ with $R^2 = 0.9975$
Wanning station	$w = 6.7422t^{0.7753}$ with $R^2 = 0.9922$

The second letter, L is the expanding direction of crack stress, means longitude. Sample and faster structure assembly according to ASTM G168 were exposed in different atmospheric environments.

2.2 Exposure environment

All specimens were exposed to two different atmospheric test stations. Wanning station, Hainan Province, located in South of China, east longitude is 110°05′and north latitude is18°58′, a marine atmosphere with high temperature and humidity, more rain and sunshine in whole year [13]. Tuandao station, Shandong Province, located in East of China, east longitude is 120°16′ and north latitude is 36°0 3′, a typical industrial pollution and marine atmosphere. It is a small island surrounding by sea, the temperature changes obviously from day to night, and air pollution is heavy, especially Cl^- is high [14]. The environmental parameters of two atmospheric stations are listed in Table 3 and Table 5.

All samples were fixed on the frame, and should be 45°angle and face to south. Exposure time for plate samples, last for 1, 2, 3 and 5 year respectively. The SCC C-ring and pre-crack specimens were exposed and removed at the time of failure, using optical check. Microstructure of surface and cross section after expose test was observed by Quanta600 SEM.

3. Resutls and Discussion

3.1 The weight loss of 7B04 aluminium alloy

Fig. 1 shows weight loss of 7B04 aluminium alloy change with exposure time in Tuandao and Wanning station.

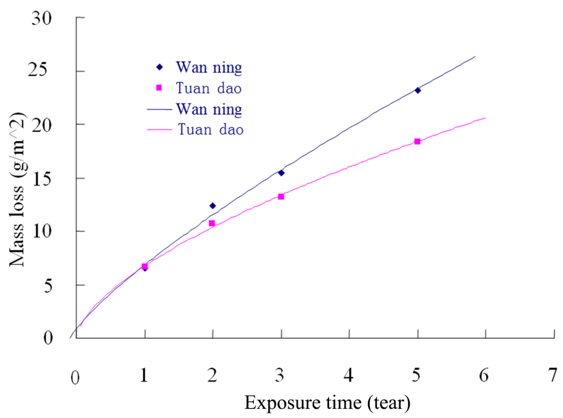

Fig. 1 Relation between 7B04 corrosion weight loss and exposure time in Tuandao and Wanning station.

Regression equation and correlation coefficient were used to analysis data of weight loss after exposing 1, 2, 3 and 5 year in order to predict corrosion severity after different exposing time. The regression curve and equation are displayed in Fig. 1 and Table 4 respectively, $w=at^b$ is a typical regression equation.

Fig. 1 shows the weight loss of 7B04 aluminum alloy during the 5-year exposure in marine atmosphere. The weight loss increases during 5-year exposure. It illustrated that weight loss of 7B04 aluminium alloy exposed in Wanning is higher than that of in Tuandao. Environmental parameters listed in Table 3 showed that the higher average temperature, average relative humidity, more wet-of-time and dew time in Wanning than in Tuandao. It is known that atmospheric corrosion is an electrochemical process which takes place under thin liquid film of electrolyte. Temperature and relative humidity are the main factors which affect the form of thin liquid film. Time of wetness (TOW), which was defined as the period during which a metallic surface was covered by adsorptive and/or liquid film of electrolyte, was another important factor that affects the corrosion of metals in atmosphere. The thin liquid film strongly depends on relative humidity. there is a critical relative humidity (CRH) below which common metals do not corrode because there is insufficient moisture to create an electrolyte film on the metal surface. In the unpolluted air, the CRH for the freshly prepared surface of aluminum is approximately 66 %. Moreover, an increase of temperature will also tend to stimulate corrosive attack by increasing the rate of electrochemical reactions and diffusion processes [8]. In other words, for a constant humidity, an increase in temperature would lead to a higher corrosion rate. Higher temperature and relative

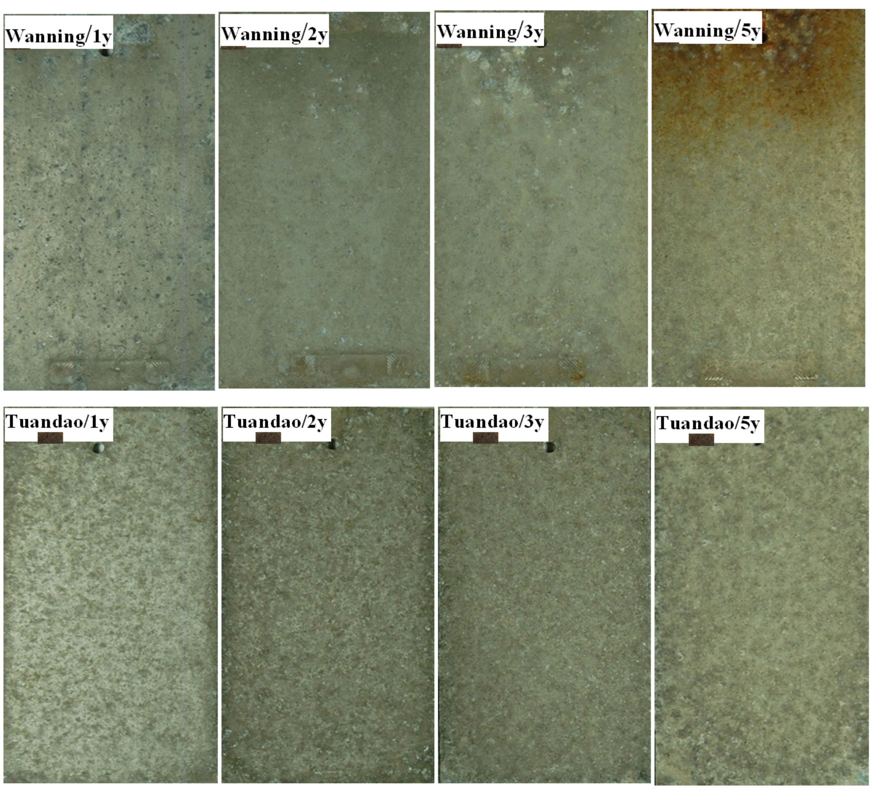

Fig. 2 Morphology of 7B04 aluminum alloy exposed in Wanning and Tuandao.

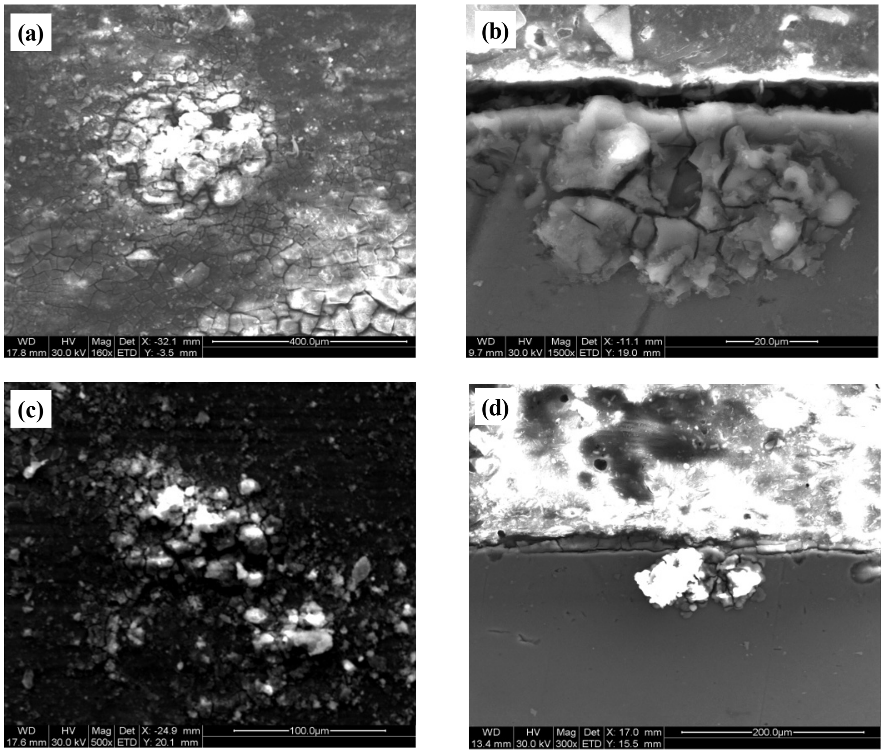

Fig. 3 SEM of 7B04 aluminum alloy specimens exposed in (a)Wanning/1y, surface(160×) ; (b)Wanning/5y, cross section (1500×) ; (c)Tuandao /1y, surface(160×) ; (d)Tuandao/1y, cross section(160×).

humidity, more wet-of-time in Wanning than in Tuandao take the dominant role in corrosion of 7B04 aluminium alloy, result that serious corrosion of 7B04 aluminium alloy in Wanning than in Tuandao.

In Table 4, w representative weight loss for per square meter, t for test time. Relative index R > 0.99 means it is very good relative formulation. Weight loss of 7B04 aluminium alloy exposed in both test sites was increased with exposure time. It is demonstrated that the accumulated role of environmental factors to corrosion for 7B04 aluminium alloy.

The function of corrosion rate is obtained by changing power function of $w=at^b$ to $\frac{dw}{dt}=a\cdot b\cdot t^{b-1}$. It is know that *dw/dt* means corrosion rate, b is small than 1 in Table 4. So that *dw/dt,* corrosion rate is decreased gradually with exposure time.

3.2 Morphology and microstructure after exposing test

The Morphologies after exposing different time in both sites were displayed in Fig. 2. It is obvious that pitting appeared at early stage of expose test, change to general corrosion with test time extension. The density of pitting on the sample surface is higher and size is smaller in Tuandao than in Wanning. Pitting still could be observed after exposure 5 years in Wanning, but general corrosion displayed evidently after exposed 5 years in Tuandao. The microstructure of cross section is showed in Fig. 3. There is still some pitting corrosion after 5 year exposing test in Wanning (Fig. 3b) comparing with 1 year exposing test in Tuandao (Fig. 3d), but pitting dose not observed after 5 year exposing test in Tuandao. It means that environmental factors in Wanning are more seriously to initial and expending of pitting. It is know that pitting is a type of localize corrosion which is heavy hazard, but could

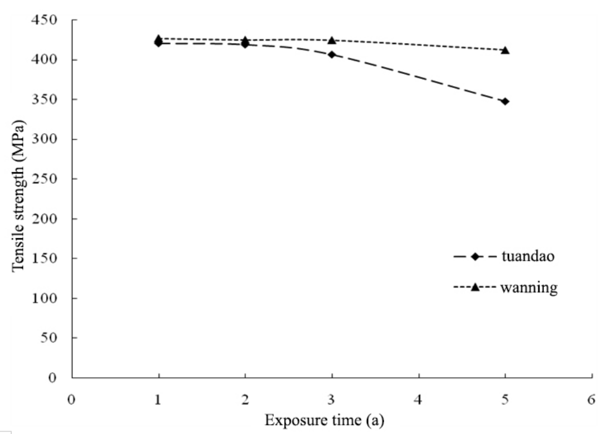

Fig. 4 Relation between tensile strength and exposure time for 7B04 aluminium alloy in Wanning and Tuandao.

not check out easily. Thin liquid layer on the 7B04 aluminum alloy exposed in Wanning is easy to be formed and sustained because of higher humidity and more time of wetness. Cl^- could be take corrosive role of for more time, it is benefit to the initial and expending of pitting. On the other hand, 7B04 aluminum alloy exposed in Tuandao could be keep dry for more time, inducing and expanding of pitting could not develop by the role of self-catalysing caused aggressive ions. It is benefit for general corrosion.

3.3 Tensile strength change with exposing time

Tensile strength of 7B04 aluminium alloy after atmospheric exposing test is showed in Fig. 4. There is not obviously decrease in 2 year exposing test. Tensile strength decreasing in Tuandao is bigger than in Wanning after 3 year exposing test. Loss of tensile strength is 17% and 3.5% respectively after 5 year compare with 1 year exposing test. This results is consistent with former's investigation [3,10]. The reason is that corrosion form changed from pitting to general corrosion after 3 year exposing, and thickness of samples was reduced, which effect on mechanical properties of sample, leading to decrease of tensile strength drastically, and early failure.

3.4 SCC results

Table 5 shows the test results which were exposed in

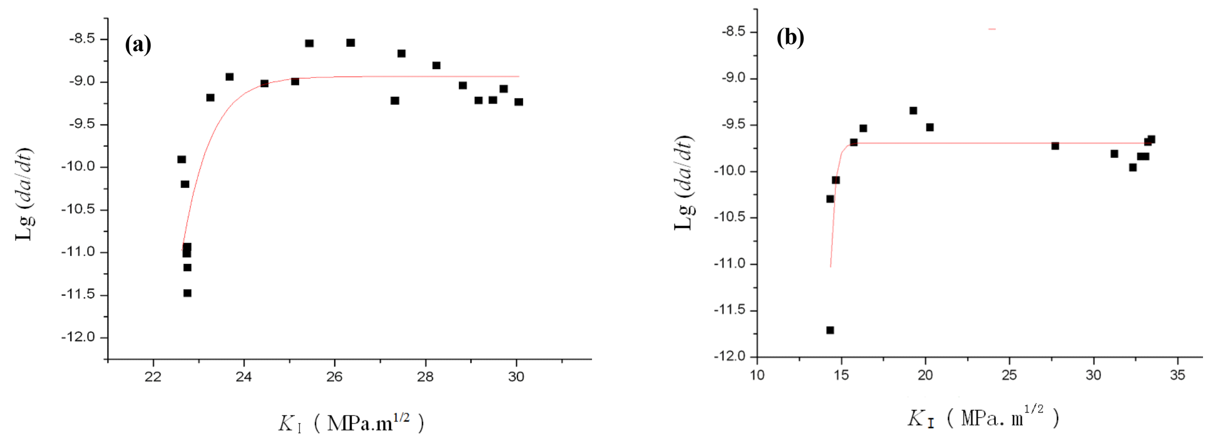

Fig. 5 The curves between cracking expanding speed and stress intensity factor 7B04 in Tuandao ; (b) 7B04 in Wanning.

Table 5 The results of C-rings samples exposed in Wanning station

identity		Thickness mm	applied stress MPa	test results		
				F/N*,	time of crack, d	average
forging	T1	78	120	2/5	612, 669	/
			140	5/5	584, 723, 594, 723, 628	650
			160	5/5	669, 619, 571, 267, 923	610
			180	5/5	537, 484, 537, 680, 680	584
plate	T1	35	120	5/5	557, 680, 680, 786, 812	703
			170	5/5	484, 557, 654, 411, 411	503
			230	5/5	252, 231, 153, 170, 110	183
	T651	55	120	5/5	605, 498, 654, 564, 564	577
			170	5/5	170, 176, 170, 176, 598	258
	T7451	50	300	1/5	991	/
			400	4/5	972, 1170, 991, 1106	1060
	T2	40	300	4/5	1160, 951, 1170, 870	1083
			400	5/5	949, 929, 993, 993, 748	922
			500	4/5	661, 661, 583, 564	617

* F-Number of the fracture sample; N--Number of the total sample

Table 6 Results of pre-crack sample exposed in wanning and tuandao

Outdoor exposure test site	K_{ISCC} / MPa·m$^{1/2}$	$(da/dt)_{II}$ / m.s^{-1}
Tuandao	20.07	1.03×10^{-9}
Wanning	11.13	3.26×10^{-10}

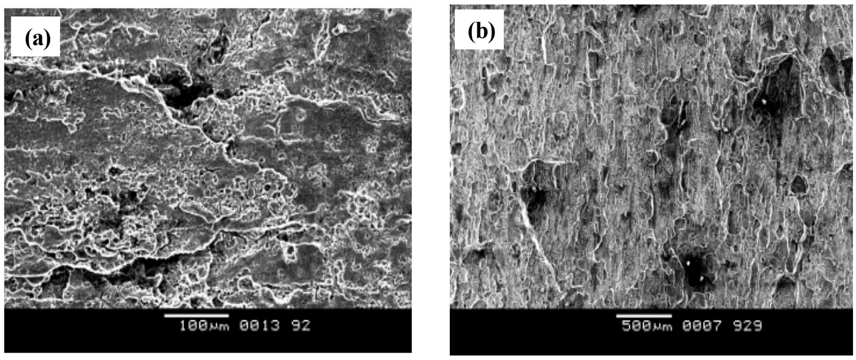

Fig. 6 Microstructure of cross-section after failure of pre-cracking specimens exposed in (a)7B04/Wanning ; (b)7B04/Tuandao.

half shelter in Wanning station. The SCC C-ring samples, taken from forging and plates with different heat treatment were applied stress before exposing test. The results show that initial crack time is decreased with the increase of level stress for both forging and plates. SCC susceptibility of 7B04 aluminium alloy is also related with heat treatment, 7B04 aluminium alloy with T7451 has lowest sensitivity to SCC, T651 is most sensitive to SCC in 7B04 plates with 4 different heat-treatment (T1, T2, T651 and T7451).

The results obtained from pre-cracking SCC specimens were showed in Table 6, the relation between cracking propagating speed and stress intensity factor was showed in Fig. 5. It is obvious that the effect of environment on the sensitivity of 7B04 aluminium alloy to SCC is remarkable. K_{ISCC} obtained from the specimen exposed in Wanning is lower than that of in Tuandao station. It is due to the effect of environmental factors and pollution in the air. Temperature and humidity are the mainly factors that effects the atmospheric corrosion, chloride as contaminant takes an important role to SCC. Higher temperature and humidity, combine the role of chloride is the reason that 7B04 aluminium alloy is more sensitive to SCC in Wanning.

The SEM results after failure of pre-cracking specimens were showed in Fig. 6, there is characteristically trans-granular mode of cracking in Wanning, intergranular or mixture mode of cracking in Tuandao, but less secondary cracking.

4. conclusion

1) The initial pitting corrosion emerges on the surface of 7B04 aluminium alloy, and transform into general corrosion later in marine atmosphere. Both the corrosion rates in Tuandao and Wanning experience a process from high to low and the mass losses vary at $w=at^b$ ($b < 1$). The corrosion of 7B04 aluminium alloy in Wanning is more serously than in Tuandao station.

2) SCC susceptibility of 7B04 aluminium alloy (forging and thick plate) is detected in marine atmosphere exposure. Higher SCC sensitivity was conducted in Wanning than in Tuandao station. SCC sensitivity is much more with higher stress level, K_{ISCC} is much difference in Wanning and Tuandao station. The intergranular, trans-granular or mixture mode of cracking can be observed in different marine exposure.

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