CORROSION SCIENCE AND TECHNOLOGY, Vol.7, No.2(2008), pp.125~129

Corrosion Behaviour of Some Alloys in Tropical Urban and Marine Atmospheres

Dang Vu Ngoan[1], Bui Ba Xuan[2,†], and Nguyen Nhi Tru[3]

[1]*Faculty of Materials Technology, The University of Technology, Ho Chi Minh City, Vietnam*
[2]*Seacoast Branch, Vietnam-Russian Tropical Centre, Nhatrang City, Vietnam*
[3]*Institute for Tropical Technology & Environmental Protection, Ho Chi Minh City, Vietnam*

Results of corrosion testing for different grades of titanium, copper, zinc, alluminium alloys and steels after two years of outdoor exposure under humid tropical urban and marine conditions have been presented and discussed. Mass loss and corrosion product characteristics for the exposed specimens at Hanoi testing site with high humidity and Nhatrang marine stations (at 100 and 1,000 meters distances from sea) with different airborne salinities (35.9 and 90.0 $mg/m^2.d$ respectively) have been selected for investigation.
From time dependence of the specimen mass loss and corrosion product characteristics, the strong influence of environmental parameters upon durability for the investigated metals and alloys has been demonstrated. Only titanium alloys show high resistance to the marine conditions. All the other specimens (copper, zinc, alluminium alloys and steels) have been underwent strong deterioration under influence of aerosol salinity. Results of corrosion products analysis have been also presented for characterization of environmental impact on the metal degradation processes.

Keywords *: alloy, corrosion rate, corrosion product, salinity*

1. Introduction

Atmospheric corrosion in tropical environment has long been a subject of great importance for material development and application. The issue has been attracted special attention in Vietnam due to its specific humid tropical climate with high concentration of airborne salinity and other industrial corrosive pollutants. Nevertheless many publications have been reported for last ten years (for example in [1- 6]), but it mainly linked with traditional metals such as mild steel, zinc, alluminium and copper. There are very few research results regarding corrosion behaviour of metallic alloys in the tropical environment.

To upgrade corrosion database of metals and alloys in the area, a long term testing programme has been setting up in different climatic regions of Vietnam since June, 2004. Different grades of titanium, copper, zinc, alluminium alloys and steels have been taken for investigation. The specimens have been tested for periods of 1, 2, 4 and 8 years of exposure.

The initial results of first 2 years of testing for these materials at 3 testing sites, representative as urban and marine environmental atmospheres, are summarised and discussed in this paper.

† Corresponding author: buibaxuan@gmail.com

2. Experimental

2.1 Environmental characteristics of the testing sites

Geographical co-ordinates and environmental characteristics of the exposure sites are shown in Table 1. Climatic parameters were measured and calculated by common meteorological methods. Airborne salinity and sulfur dioxide depositions were determined by wet candle and passive specimen methods respectively. All the values are the average for last two years. Hanoi is classified as urban tropical climatic zone with high value of ambient temperature, air humidity, time of wetness and high concentrations of pollution. Nhatrang site is mainly influenced by marine climate with high sunshine time and high solar radiation.

2.2 Test specimens and testing procedure

Specimens with dimension 100x150x1-3 mm were prepared according to ISO DIS 8565. Three parallel specimens for each material have been taken for periods 1, 2, 4, 8 years outdoor exposure. The blank specimen has been

Table 1. Environmental characteristics of the testing sites

Parameter / Site	Hanoi urban	Nhatrang urban	Nhatrang seashore
Latitude/longitude	21°01N, 105°48E	12°15N, 109°11E	12°15N, 109°12E
Distance from the sea, *km*	~ 100	1.0	0.1
Altitude, *m*	5.97	2.98	6.5
Average temperature, ℃	24.5	27.6	27.9
Average humidity, %	79.0	75.4	76.0
Time of wetness, *h/year*	4666	3799	3932
Cl^-, $mg/m^2.d$	0.48	35.9	90.0
SO_2, $\mu g/m^2.d$	8.44	2.51	2.05

stored in desiccators for comparison. The specimens have been exposed in unsheltered condition facing to the south under an angle 45^o.

The specimen surfaces were pretreated following common standard before exposition. Corrosion products were cleaned by mechanical and chemical methods described in ISO DIS 8407. Mass loss was determined by weighing with accuracy 0.0001 g at temperature 27-28℃ and relative humidity 70-75%. The results were filed from average values of three specimens weight. The corrosion rates C were estimated as follows:

C (g/year) = mass loss (g)/duration of the exposure(year) (1)

The treatment of specimens before and after exposure was conducted according to standards. Crystalline phases of corrosion products were identified by XRD method and Fourier transform infrared reflection absorption spectroscopy (FTIR-RAS) was applied to examine non-crystalline corrosion products. Chemical content of testing materials are describing in Table 2. The alloy grade is referred to Russian system of standard classification.

3. Results and discussion

3.1 Corrosion rate and corrosivity of the atmosphere

Corrosion rates of the investigated metals and alloys after first 2 years of testing are presented in Table 3 and

Table 2. Chemical contents of the tested materials

No	Test materials	Alloy content (%)
1	Alluminium A5	99.5Al, <0.2Fe, <0.2Mn, <0.1Ti, <0.2Mg, <0.1Ni, <0.1Si, <0.2Zn, <0.2Cu.
2	Alluminium alloy D16	Al, 0.30Fe, 0.40Mn, <0.2Ti, 1.77Mg, <0.2Ni, <0.2Si, <0.2Zn, 4.68Cu.
3	Alluminium alloy AMg3M	Al, <0.2Fe, <0.3Mn, <0.2Ti, 3.68Mg, <0.2Ni, 0.58Si, <0.2Zn, <0.2Cu.
4	Brass BrKMSJ-1	Cu, <0.3Sb, <0.3Pb, <0.3Zn, <0.3Sn, 3.03Si, 0.04Fe, <0.3Al, 0.007Ni, 1.03Mn.
5	Bronze L63	Cu, <0.2Sb, 0.034Pb, <0.2Sn, 0.04Fe, <0.2Al, <0.3Ni, Zn % remain
6	Copper M3	99.5Cu, <0.1Sb, 0.013Pb, <0.005As, <0.1Zn, 0.014Sn, 0.035Fe, 0.02Ni, <0.002Bi ;
7	Steel St 3SP	Fe, <0.3Ni, <0.3Cr, 0.56Mn, <0.3Al, 0.15Si, <0.2Ti, <0.2V, <0.3Mo, <0.3Nb, <0.3Cu, <0.3W, 0.150C, 0.019S.
8	Steel St 08 KP	Fe, <0.3Ni, <0.3Cr, <0.3Mn, <0.3Al, <0.1Si, <0.2Ti, <0.2V, <0.2Co, <0.3Mo, <0.3Nb, <0.3Cu, <0.3W, 0.074C, 0.033S.
9	Steel 30 KHGSA	Fe, <0.3Ni, 1.09Cr, 0.98Mn, <0.3Al, 1.14Si, <0.1Ti, <0.1V, <0.3Co, <0.3Mo, <0.3Nb, <0.3Cu, <0.3W, 0.31C, 0.005%S.
10	Steel 12KH 18N 10T	Fe, 10.6Ni, 17.7Cr, 1.28Mn, <0.3Al, 0.30Si, 0.72Ti, <0.3V, <0.3Co, <0.3Mo, <0.3Nb, <0.3Cu,<0.3W, 0.092C, 0.007S.
11	Titanium alloy VT-20	Ti, <0.3Fe, 1.62V, 6.11Al, <0.2Mn, <0.2Cr, 2.03Zr, <0.2Si, <0.2Ni, 1.33Mo, <0.2Sn, <0.2Nb, <0.2%Cu.
12	Titanium alloy OT-4	Ti, <0.3Fe, <0.3V, 3.54Al, 1.43Mn, <0.2Cr, <0.3Zr, <0.2Si, <0.2Ni, <0.2Mo, <0.2Sn, <0.2Nb, <0.2Cu.
13	Zinc SOA	99.98Zn, <0.0004B, <0.0004Na,<0.0001Mg, <0.0002Al, <0.006K, <0.0004Ca, <0.00004Sc, <0.00007Ti, <0.00007V, <0.00008Cr, 0.0075Pb, 0.00002Mn, 0.00066Fe, 0.000027Co, <0.00006Ni, <0.0009Cu, <0.000009Ga, <0.00001As, <0.0002Se, <0.000004Rb, <0.0000008Zr, <0.0000005Nb, <0.000006Mo,<0.000003Pd, 0.00033Ag, 0.0003Cd, <0.00008Sn, <0.00003Sb, <0.00001Te, <0.000001Cs, <0.000009Ba, <0.0000003Ta, <0.000007W, 0.000003Bi.

Table 3. First year corrosion rates for metals and alloys at different sites

No	Materials	First year corrosion rate, $g/m^2.y$		
		Nhatrang urban	Nhatrang seashore	Hanoi urban
1	Alluminium A5	0.12	1.08	0.06
2	Alluminium alloy D16	0.28	1.39	0.07
3	Alluminium alloy AMg3M	0.47	1.27	0.08
4	Brass BrKMSJ-1	14.57	44.3	10.2
5	Bronze L63	2.53	3.52	10.8
6	Copper M3	9.67	35.8	10.3
7	Steel St 3SP	126.4	253.3	127.7
8	Steel St 08 KP	120.8	349.0	140.8
9	Steel 30 KHGSA	130.8	251	121.6
10	Steel 12KH 18N 10T	0.23	2.1	0.46
11	Titanium alloy VT-20	0.0114	0.020	0.008
12	Titanium alloy OT-4	0.0100	0.013	0.009
13	Zinc SOA	8.78	21.3	4.5

Table 4. Second year corrosion rates for metals and alloys at different sites

No	Materials	Second year corrosion rate, $g/m^2.y$		
		Nhatrang urban	Nhatrang seashore	Hanoi urban
1	Alluminium A5	0.095	0.665	0.04
2	Alluminium alloy D16	0.155	0.65	0.04
3	Alluminium alloy AMg3M	0.245	0.65	0.045
4	Brass BrKMSJ-1	11.45	34.15	9.65
5	Bronze L63	3.05	3.85	6.0
6	Copper M3	6.1	20.35	6.5
7	Steel St 3SP	95.0	211.6	125.1
8	Steel St 08 KP	102.0	270.0	124.5
9	Steel 30 KHGSA	80.0	183.3	102.5
10	Steel 12KH 18N 10T	0.165	1.45	0.37
11	Titanium alloy VT-20	0.0113	0.015	0.03
12	Titanium alloy OT-4	0.0105	0.020	0.0065
13	Zinc SOA	6.7	15.0	6.65

Table 4. At first glance, it is clear that corrosion rate of titanium alloy is negligible for 3 testing sites, while all other metals and alloys are undergone severe damage in severe tropical conditions.

Differing from first year results, corrosion rate of second year exposure is sharply decreased for all grades of alloys. However, behaviours for different alloys are differently expressed. In comparison with pure metal, alluminium alloys are quite stable in urban condition. With increasing of airborne salinity, corrosion rates of these alloys are increased many times. Among copper alloys, only bronze L63 is higher corrosion resistant than its pure metal, while brass BrKMSJ-1 is damaged severely in tropical atmospheres. As in case of alluminium, similar corrosion rate tendency of copper and zinc alloys in relation with increasing airborne salinity. For copper M3, brass BrKMSJ-1, some grades of steels, when airborne salinity increases 3 times (35.9 to 90 $mg/m^2.d$ for Nhatrang urban and seashore site respectively), corrosion rates also increased approx. 3 times see Table 3). Considering the similar other metrological conditions, it can be concluded that airborne salinity plays major role in corrosion promoting.

Another corrosion behaviour occurs for tested grades of steels. In Hanoi urban condition with high time of wetness and high atmospheric sulfur dioxide content, corrosion rates in most cases are comparative with the values in Nhatrang urban site specified by higher airborne salinity. While airborne salinity still plays role in promoting corrosion, the influence of sulfur dioxide in humid tropical environment is prevailing for most grades of steel except Steel 12KH 18N 10T.

Based on first year corrosion rates of standard specimens, the atmospheric corrosivity of the sites for the investigated metals can be classified according to ISO 9223. The classification results are presented in Table 5. The obtained data show that Hanoi and Nhatrang urban atmospheres are moderately corrosive for all grades of alloys, while Nhatrang seashore atmosphere is high corrosive, especially for nonferrous metals. This classification once more shows the predominating effect of airborne salinity on corrosion of the metals and alloys.

3.2 Surface appearance and corrosion products

Surface appearance of alloys, exposed in Nhatrang conditions for 2 years, are described in Table 6. Specimen images show visible influence of marine climate on the corrosion behaviour of alloys. These are very similar to the results reported by the authors [3] to [5] for zinc, copper and alluminium alloys respectively.

Reasons of surface appearance colour changes are due to complicated process of corrosion product transformation during exposure period. Different crystal or amorphous phases of these products have been formed on the specimen surfaces would be very specific indicators for corrosive atmospheres.

Influences of airborne salinity and sulfur dioxide is more clearly shown considering the chemical composition of corrosion products in Table 7 after 2 years of exposure. Some conclusions can drawn from analysing the crystal phases of specimens exposed at different sites of Nhatrang and Hanoi.

For copper alloys some in Nhatrang urban and marine sites, brochantite was found as a trace only on the skyward side of the 2-year specimens. Thus, chloride hinders the formation of brochantite. Nantokite was the most fairly frequent chlorine-containing product in all atmospheres. For steels acaganeite was formed in marine atmosphere with abundant airborne salinity, while goethite and lepidocrocite generally occur in corrosion products for all sites.

Simonkolleitte is a major crystal phase in zinc corrosion product formed in marine conditions while zinc hydrosulfate, zinc oxysulfite are very popular for urban-industrial environments.

Table 5. Classification of atmospheric corrosivity according to ISO 9223

TT	Materials	Testing site		
		Nhatrang urban	Nhatrang seashore	Hanoi urban
1	Alluminium	C2	C3	C2
2	Copper	C3	C5	C3
3	Steel	C3	C3	C3
4	Zinc	C3	C4	C2

Table 6. Description of alloy surface appearance in Nhatrang atmosphere after 2 year of exposure

No	Materials	Side	Appearance
1	Alluminium and alloys	Skyward	Dark surface with white spots 3-4 mm for alluminium. Grey corrosion product for D16 grade of alloy. Less dark colour for AMg3M alloy
		Groundward	More dark surface without white spot for alluminium. More grey corrosion product for D16 grade of alloy. Less dark colour for AMg3M alloy
2	Copper and alloys	Skyward	Spots with red-purple or red brown colour. They turned to greenish-grey after 1 year of exposure. The skyward side was always darker than the groundward side.
		Groundward	Spots with red-purple or red-brown colour. They turned to greenish-grey after 1 year of exposure. Groundward side is darker for brass BrKMSJ-1
3	Zinc alloy	Skyward	Grey corrosion products on skyward side. Surface is roughly corroded forming a group of grey spots throughout the specimen surface
		Groundward	More dark on grounded side, especially at bottom of specimens. The corrosion products are more porous than on the skyward side.
4	Mild steels	Skyward	Porous red-brown corrosion products. High roughness of the surfaces.
		Groundward	Porous red-brown corrosion products. High roughness of the surfaces.

Table 7. The crystal phases in corrosion products

TT	Materials	Crystal phases in corrosion products at		
		Nhatrang urban	Nhatrang seashore	Hanoi urban
1	Copper and alloys	Cuprite (major), langite, posnjakite, brochantite, copper hydroxide, nanokite, atacamite	Cuprite (major), posnjakite, brochantite, botallackite, atacamite	Cuprite (major), langite, posnjakite, brochantite (minor), copper hydroxide, nanokite
2	Steels	Goethite, lepidocrocite, magnetite, acaganeite	Goethite, lepidocrocite, magnetite, acaganeite	Goethite, lepidocrocite, magnetite.
3	Zinc alloy	Zinc hydroxide, zinc carbonate, hydrozicite, simonkolleitte	Simonkolleitte (major), Zinc hydroxide, zinc carbonate, hydrozicite,	Zinc hydroxide, zinc carbonate, zincosite, zinc hydrosulfate, zinc oxysulfite

4. Summary

1) Nhatrang seashore environment is very corrosive for all metals and alloys especially for nonferrous metals. Corrosion rates at this area are several times exceed the values obtained for Hanoi urban atmosphere.

2) Airborne salinity is a main factor accelerating corrosion for nonferrous metals and alloys in Nhatrang conditions. In contrary, sulfur dioxide is a reason causing corrosion damage for steels in Hanoi urban atmosphere.

3) The initial corrosion rate filing data can be served as good reference results to select suitable alloys for application in different climatic zones of humid tropical area.

References

1. I. S. Cole, A. K. Neufeld, P. Kao, W. D. Ganther, I. Chotimongkol, C. Bhamornsut, Nguyen V. Hue, Nguyen N. Tru, S. Bernado, S. Purwadaria, *Proc. of the 11th APCCC,* p.555, Vietnam (1999).
2. Nguyen viet Hue, I. S. Cole, Vo De, Bui Van Thao, Nguyen Nhi Tru, Truong Dinh Mau, W. Ganther, A. Neufeld (1999), *Proc. of the 11th APCCC,* p.582, Vietnam (1999).
3. Le Thi Hong Lien, "Corrosion of zinc coatings in Vietnam atmospheric environments", *Ph. D. Thesis*, Vietnam Academy of Science & Technology (2005).
4. Tran Thi Ngoc Lan, "Environmental Characteristics and Materials Damage in Soth Vietnam", *Ph. D. Thesis*, Osaka prefecture University (2004).
5. Nguyen Duc Hung, Tran Van Chung, Le Quang Tuan, *Proc. of the 16th ICC*, paper 05-B-36, Beijing (2005).