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Effect of biofouling on corrosion behaviour of grade 2 titanium in Mandapam seawaters

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Abstract

Titanium has the ability to withstand extremely high seawater velocities with negligible corrosion. The inherent passive nature of the metal favours the attachment of bio-organisms more. In this paper the biofouling characteristics and the influence of macrofouling on grade 2 titanium have been investigated in the Palk Bay waters of Mandapam (India) over a period of a year.This work comprises both field exposure as well as laboratory studies. The deposits on titanium were analyzed with the XRD technique. Green algae such as *Cladophorapsis zoolengeri*, *Cheatomorpha area*, *Chlorodesmis hillibrandii*, *Enteromorpha intestinalis*, *Cladophora* species and red algae species of *Hypnea valentiae*, and animals such as bryozoans and barnacles 4 mm in size were identified on the titanium metal surface. The effect of macrofouling on corrosion of titanium was investigated by both impedance and polarization techniques. Titanium experienced negligible corrosion in seawater exposure with an appreciable fouling load of 0.4527 $kg.m^{-2}y^{-1}$.

Keywords: Biofouling; AC impedance; XRD technique

1. Introduction

Titanium alloys in seawater are passive and are most unlikely to suffer any form of corrosion [1]. It also has the ability to withstand extremely high seawater velocities with negligible attack [2]. It is an excellent material for applications involving handling of hot seawater in desalination and cooling water systems. Titanium has n-type semiconducting oxide film, which has a crystalline form (rutile) or amorphous form (anatase). Mandapam is a shallow coast and sunlight can easily activate the oxide film in daytime, which can enhance the production of H_2O_2 on the metal surface. Titanium corrosion resistance relies upon the formation of a very thin oxide film, which occurs spontaneously in air or water. As long as

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this oxide film remains passive, corrosion rates for titanium will be insignificant.

Hutchinson and et al. [3] reported on the apparent immunity of titanium to seawater by atmospheric jet impingement and seawater immersion tests. These results were confirmed by Williams [4] along with additional information. Exposure up to 8 months in the atmosphere, in quiescent and rapidly moving seawater and on jet impingement had a negligible effect. LaQue [5] reported similar results for titanium exposed to marine environment for extended periods of time under marine test condition. Titanium alloys are immune to localized corrosion in seawater under ambient conditions and show little if any ennoblement [6].

In spite of titanium's excellent corrosion behaviour, three problem areas pertaining to marine environments have been encountered [7]: (1) corrosion pitting observed at oxygen starved crevices when the seawater is heated to 250°F and above, (2) stress corrosion cracking in the presence of tensile stresses and a surface flaw and (3) stress corrosion cracking when stressed salt contaminated titanium is heated to 500°F or higher. Titanium and its alloys are excellent materials for applications involving handling of hot seawater in desalination and hot brines in the chemical industry. The main applications of the grade 2 titanium are high pressure heat exchangers and piping systems in seawater desalination plants, offshore technology, and chemical and petrochemical plants [8,9]. Hence corrosion resistant material, grade 2 titanium, has been selected in this study with respect to the fouling and electrochemical behaviour in the seawater.

2. Experimental

Mandapam is a shallow, rocky coast, rich in algal flora and calcareous growth, particularly barnacles and corals. The exposure site has been selected for the present study is in the Palk Bay of Mandapam (longitude 79°8″ east; latitude 17″ north). The SW and the NW monsoons prevailing during the periods April–August and November–February respectively influence climate in Mandapam. The existence of monsoon causes striking variations in the water characteristics at a site during different parts of a year and during the entire year between the Gulf of Mannar and Palk Bay. For instance, the seawater at Palk Bay is rough during the northeast monsoon whereas the one at Gulf of Mannar is calm. The reverse happens when the southwest monsoon takes over. Fouling therefore is very much influenced by the monsoon period since water currents determine the type of larval or spores being transported. The seawater characteristics are given in Table 1.

Table 1
Seawater characteristics of Palk Bay at Mandapam coast (October 1996–September 1997)

Characteristics	Max.	Min.	Ave.
Surface temperature, °C	31.2	26.4	28.8
Salinity, ppt	35.0	25.6	30.3
Dissolved oxygen, ml/l	5.0	2.8	4.2
Calcium, mg/l	332	329	331
Magnesium, mg/l	1173	1158	1166
Carbonate, mg/l	20.5	15.4	18.0
Bicarbonate, mg/l	115	105	110
Sulfate, mg/l	2165	2153	259
pH	8.3	8.1	8.2

2.1. Material

Specimens of grade 2 titanium, size 150 mm× 25 mm × 1 mm with the following compositions were used.

- Fe: 0.30%
- C: 0.10%
- N: 0.03%
- Titanium: balance

The specimens were pickled in respective cleaning solutions [10] and polished and holes were provided on the top and bottom end of the peripherals of each panel. Duplicate panels were fixed in conventionally designed wooden racks using brass bolts and nuts where metal-to-metal and metal to wood contacts were prevented using polyethylene insulation. The wooden racks fitted with panels were tied to the stationery piles in the Palk Bay waters of Mandapam, India, about 0.5 M below the mean sea level in order to effect the total immersion of the test specimens during the study period. The exposure tests were conducted monthly, quarterly, half yearly, nine months and yearly. After retrieval, the panels were examined for the presence of fouling organisms.

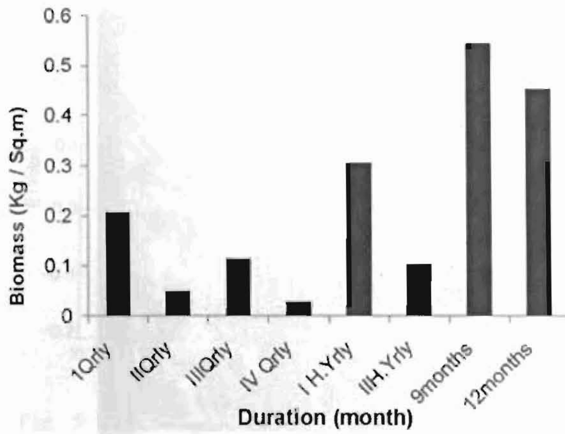

Fig. 1. Fouling pattern of titanium.

2.2. *Laboratory studies*

Coupons in duplicate sizes 5 cm × 2 cm were employed for macrofouling studies. The studies were carried out both in natural seawater and in sterilized seawater for 3 months and 6 months respectively. Both DC polarization and EIS measurements were carried out in a three-electrode cell consisting of working electrode, platinum auxiliary electrode and saturated calomel electrode using an Electrochemistry System (Solarton 1280B), and PAR Impedance Analyzer (6310) respectively.

The metals after respectives period of exposure were removed from the seawater and dried in an air oven at 60°C for an hour. Then the deposit was scraped from the respective panels and finely powdered. XRD studies were made (JDX8030) to identify the constituents of respective deposits.

3. Results and discussion

3.1. *Fouling production and community development pattern*

The general fouling organisms of the Mandapam coast, particularly in Palk Bay waters, are algae, bryozoans, barnacles and molluscs. Fig. 1 gives the fouling pattern on titanium. Green algae such as *Cladophorapsis zoolengeri*, *Cheatomorpha area*, *Chlorodesmis hillibrandii*, *Enteromorpha compressa*, *Enteromorpha intestinalis* and *Cladophora* species were recorded in monthly exposure panels. Red algae species of *Hypnea valentiae* and blue-green algae species of *Lyngbya majescula* were also recorded. Animal species of barnacles and bryozoans were recorded. Species of *Cladophora*, *Cheatomorpha area*, *Enteromorpha intestinalis*, *Chlorodesmis hillibrandii*, *Cladophorapsis zoolengeri*, and *Centroceras clavulatum* were recorded in quarterly exposed panels. Dense mat of barnacles of size 4 mm were recorded in yearly exposed panels, with a biomass of 0.4527 kg.m^{-2}

The fouling load is the least in Mandapam, which is equal to the fouling load of copper at Tuticorin waters [11]. It can also be explained that the fouling load reveals the potential of the site and it can be assumed that the physical characteristics of the sea, viz wave and tide, may determine the wealth of the site. The surface appearance after exposure in natural seawater for the periods of 6 and 12 months is shown in Figs. 2 and 3. It was observed that the surface of 6-month exposed panels experienced fouling with barnacles, and the surface of 12-month exposed

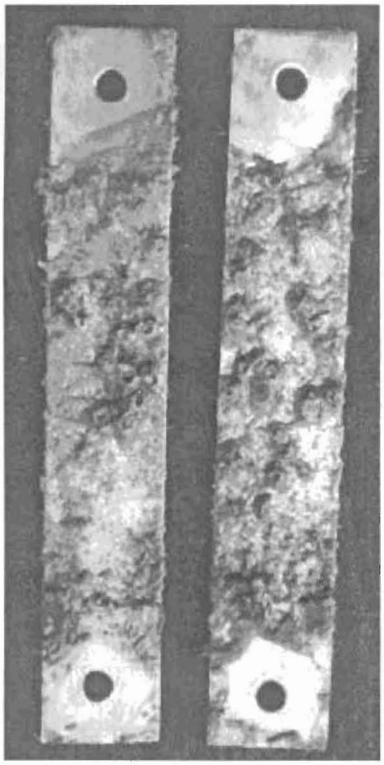

Fig. 2. Surface appearance of half yearly exposed titanium in natural seawater.

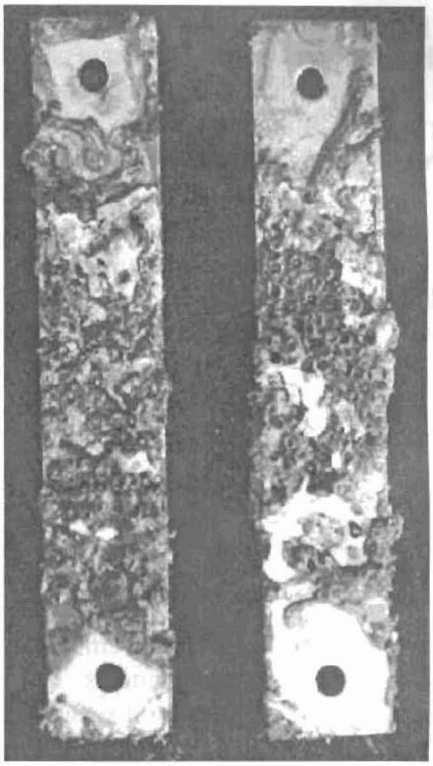

Fig. 3. Surface appearance of yearly exposed titanium in natural seawater.

panels experienced with a dense mat of barnacles 2 mm in size. Recent studies have shown that particularly in the coral reef environment in the Red Sea, various Chromista settlements, especially diatoms, were observed [12].

3.2. Corrosion behaviour of titanium

Both monthly exposure and cumulative exposure of titanium in natural seawater at Palk Bay experiences very low corrosion throughout the study periods. Even under the most aggressive conditions that existed during December 1996 and January 1997, and also under the presence of heavy growths of barnacles and algae, adhered onto the metal surface, they do not promote pitting or other types of corrosion of the metal. Figs. 4–7 show the polarization behaviour of titanium in natural seawater and sterile seawater media for the period of 3 months and 6 months respectively. Table 2 gives the electrochemical parameters obtained by Tafel polarization for titanium due to macrofouling. In the 3- and 6-month exposure periods, the I_{corr} values of grade 2 titanium in natural seawater are in the range of 0.22 and 0.25 μA.cm^2, while the I_{corr} values in sterilized seawater are in the range between 0.027 and 0.065 μA.cm^2.

The lower corrosion current values in the sterilized seawater may be due to the case of passive film formation in comparison with that of natural seawater in which the oxygen supply to the metal surface is restricted by the affected biospecies. Besides, the polarization curves indicate the lower passivation current in sterile seawater in comparision to that of natural seawater.

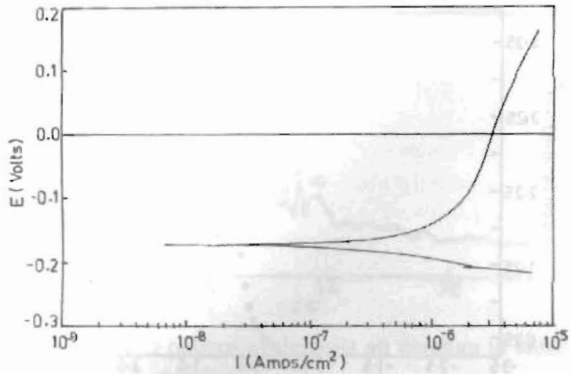

Fig. 4. Polarization behaviour of titanium in natural seawater (3 months).

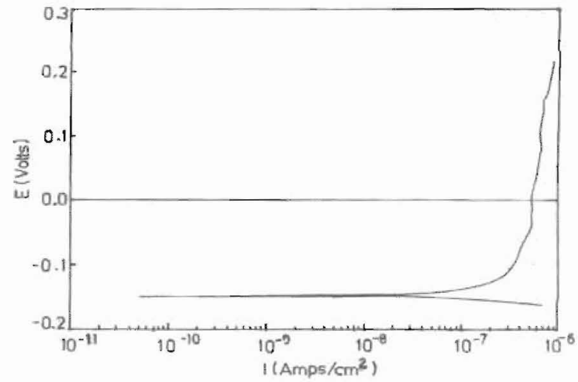

Fig. 5. Polarization behaviour of titanium in sterile seawater (3 months).

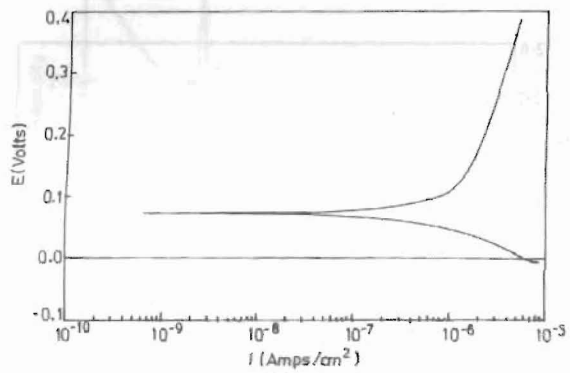

Fig. 6. Polarization behaviour of titanium in natural seawater (6 months).

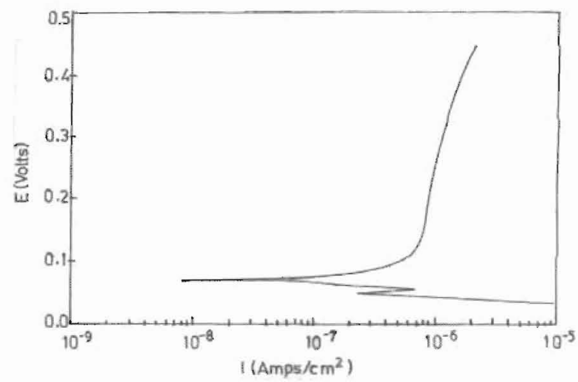

Fig. 7. Polarization behaviour of titanium in sterile seawater (6 months).

Table 2
Polarization parameters for titanium in natural seawater (NSW) and sterile seawater (SSW)-macrofouling

Medium	Sl. no.	Duration (months)	E_{corr}, mV	I_{corr} μA, cm^2	*ba*, mV/dec	*bc*, mV/dec	Corrosion rate, mmpy
NSW	1	3	-175	0.22	—	—	0.0037
	2	6	-71	0.26	66	48	0.0044
SSW	1	3	-145	0.027	13	19	0.0005
	2	6	-70	0.065	19	17	0.0011

It is clear from the table that the I_{corr} values are low in sterile seawater exposure compared to natural seawater exposure. But the E_{corr} value is slightly higher in the 3-month period of exposure in natural seawater. After the 6-month period the E_{corr} values are identical in both the media of exposure.

Videla et al. [13] reported that the biofouling species hinder passivation by retarding the transport of chemical species able to cause passi-

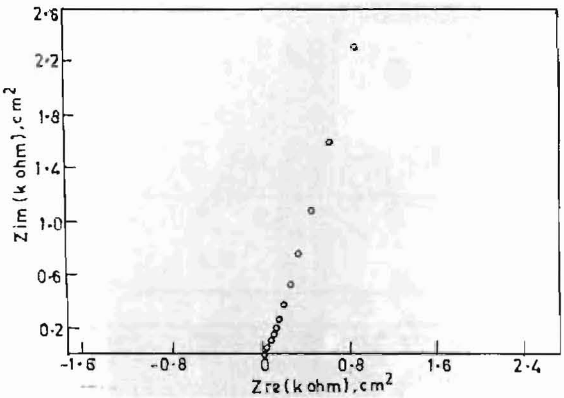

Fig. 8. Impedance behaviour of titanium in natural seawater (3 months).

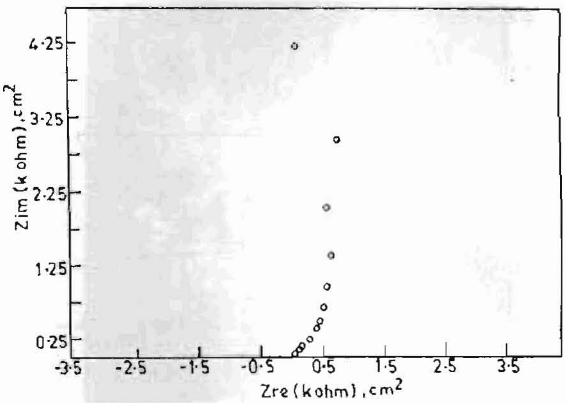

Fig. 9. Impedance behaviour of titanium in sterile seawater (3 months).

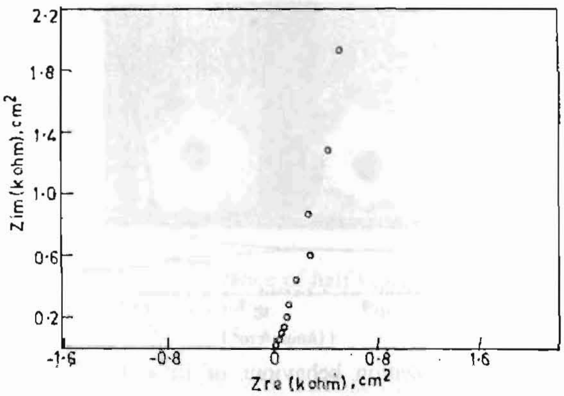

Fig. 10. Impedance behaviour of titanium in natural seawater (6months).

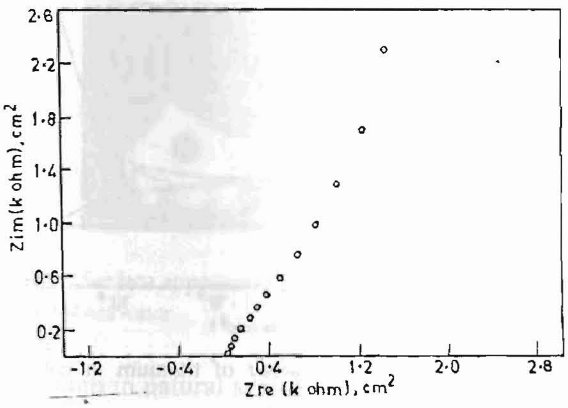

Fig. 11. Impedance behaviour of titanium in sterile seawater (6 months).

vation. From that it is inferred that the passivating film disturbances causes the rate determination in the system. Both the systems exhibit ennoblement behaviour and the values vary between −175 to 71 mV in natural seawater exposure and −145 to −70 mV in sterile seawater exposure. There is no corrosion loss in the polarization technique which is confirmed by the weight loss technique. It can be assumed that the higher corrosion current in natural seawater may be due to the attachment of macrofouling organisms in the latter period.

Figs. 8–11 show the impedance behaviour of titanium in natural seawater and sterile seawater for the period of 3 and 6 months, respectively. The capacitative nature of impedance data shows that the titanium is passive in both media. The presence of passive film in both the media has also been confirmed by polarization studies. Figs. 12–14 show the XRD pattern of deposits formed on titanium in natural seawater for 3-month, 6-month and 12-month periods of exposure. The most predominant peak in the one-year sample is at 29.3° with d values of 3.046°A, which corresponds to calcium carbonate in calcite form. The half yearly products show predominant peaks at 29.5° corresponding to d = 3.348 and

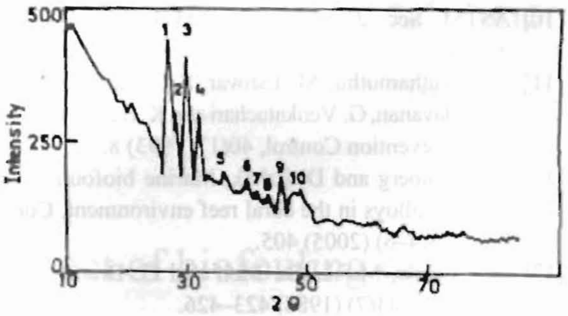

Fig. 12. XRD pattern of deposits on titanium in natural sea water (3 months).

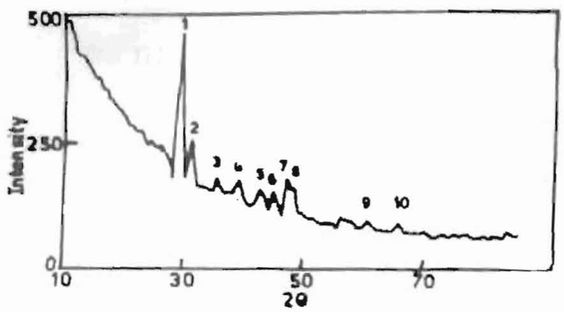

Fig. 13. XRD pattern of deposits on titanium in natural sea water (6 months).

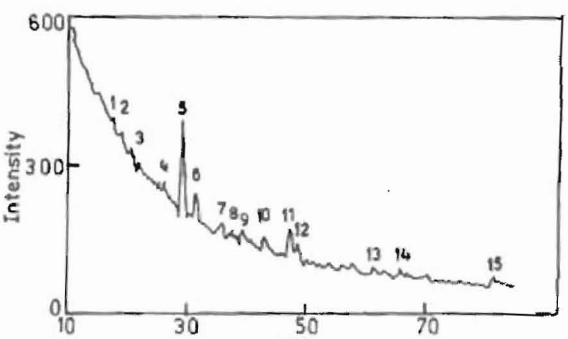

Fig. 14. XRD pattern of deposits on titanium in natural seawater (12 months).

29.4° with $d = 3.025$ respectively. It is observed that quarterly and half yearly exposed panels contain H_2TiO_3 and TiO. The yearly exposed panel shows the presence of calcareous deposits in the form of $CaCO_3$.

Corrosion of unalloyed titanium in ambient seawater of shallow condition is 8×10^{-7} mmpy [14]. Due to passive nature of titanium, corrosion rates are typically much lower than 0.04 mmpy well below the 0.13 mmpy maximum corrosion rate commonly accepted by designers. A comparative analysis of the performance of titanium in the natural seawater of Kure Beach, N.C., flowing at 3 ft/s. in a trough was nil for 483 days of exposure and also in 618 days of exposure. Similar results were observed for materials exposed for 480 days in quiet seawater in the basin at Kure Beach [2] whereas the same metal exposed for 120 days of exposure at the same site showed no measurable weight loss [3]. It is evident that the corrosion behaviour of titanium in Mandapam Palk Bay waters is identical to that of Kure Beach, N.C.

4. Conclusions

1. Both monthly and cumulative exposure of titanium metal to natural seawater showed nil corrosion.
2. Electrochemical studies showed that biofouling did not affect passivity of titanium in seawater.
3. The fouling load was found to be 0.45 kg $m^{-2}\,y^{-1}$.

References

[1] R.W. Schutz and D.E Thomas, Corrosion of titanium and titanium alloys, in: Corrosion, Vol. 13, ASM HandBook, ASM International, Materials Park, OH, 1987, pp. 676–677.
[2] H.B. Bomberger, P.J. Cambourelis and G.E. Hutchinson, Corrosion properties of titanium in marine environments, J. ElectroChemical Soc., 101(9) (1954) 442–447.
[3] G.E. Hutchinson and P.H. Permer, Corrosion, 5 (1949) 319.
[4] W.L. Williams, US Engineering Experimental Station Report C-3395, C-3501B.

[5] F.L. LaQue, Engineering Research and Development Laboratory Symposia, Fort Belvoir, Virginia, 1952, p. 55.
[6] B.J. Little, P.A. Wagner and R.I. Ray, Corrosion/93, Paper No. 308, NACE, 1993.
[7] N.G. Feige and T.J. Murphy, Environmental effects on titanium alloys, Corrosion, 22(11) (1966) 320–324.
[8] N.A. Waterman and M.F. Ashby, Elsevier Materials Selector, Vol. 2, Elsevier Applied Science, London, 1991, pp. 1217–1257.
[9] L. Plaza and A. Mand Irisarri, Maneles Mecanica Fracturu,Vol. 10, Marido, 1993, p. 306.
[10] ASTM, Sec. 2, V02.04, ASTM B600-91, 2001, p. 569.
[11] S. Maruthamuthu, M. Eshwar, S.T. Manickam, S. Ambalavanan, G. Venkatachari and K. Balakrishnan, Corr. Prevention Control, 40(1) (1993) 8.
[12] T. Greenberg and D. Itzhak, Marine biofouling of titanium alloys in the coral reef environment, Corr. Rev., 23(4–6) (2005) 405.
[13] H.A.Videla, M.F.L. De Melf and G. Brankevich, Corrosion, 44(7) (1988) 423–426.
[14] ASM Handbook, Korb, Metals HandBook, 9th ed., Corrosion of Titanium and Titanium Alloys, Vol. 13, 1987, p. 677.