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# Studies on Breakdown of Passivity of Titanium covered with *in vitro* Biofilms

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## ABSTRACT

This paper presents the influence of pure biofilms of sulfate reducing bacteria (SRB) and heterogeneous biofilms of SRB and manganese oxidizing bacteria (MOB) on the passivity of titanium. Two to eight weeks old SRB biofilm and 12 week old heterogeneous biofilms with SRB and MOB were developed on titanium. Epifluorescence microscopy, scanning electron microscopy, X-ray diffraction and X-Ray Photoelectron spectroscopy were used to characterize the biofilms. Cyclic polarization experiments were conducted in natural sea water with pure and heterogeneous biofilms. These biofilms breakdown the passive film leading to localized corrosion and a probable mechanism of passivity breakdown is proposed.

JCSE The Journal of Corrosion Science and Engineering
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**Keywords**: titanium, polarization, microbiological corrosion, passivity, Sulfate Reducing Bacteria (SRB), Manganese Oxidizing Bacteria (MOB).

## Introduction

Water is one of the most common heat transfer fluids and most of the problems associated with corrosion and deposits are water-related. If long term reliability of heat transfer equipment has to be achieved, the mechanism of microbiologically influenced corrosion (MIC) and fouling has to be understood. It is well known that sulfate reducing bacteria (SRB) are found in marine and freshwater sediments where sulphate is present. They have also been commonly isolated from industrial water systems such as cooling waters and oil fields [1, 2]. They were considered as the major bacterial group involved in MIC [3]. The open cooling systems are particularly suitable for the activities of SRB, because they handle large volumes of water which is maintained at the temperature range of 30 to 60°C with pH of 6-9, and provide a continuous source of bacteria from make-up water and ambient air. For metabolic activities, SRB utilize sulphate as an electron acceptor and produce $H_2S$ [3, 4]. $H_2S$ directly attacks metal surfaces and causes corrosion of various metals including carbon steels, stainless steels, and copper alloys [1]. When materials are exposed to cooling waters, aerobic microbes attach and form biofilms. Underneath these biofilms, as the oxygen content decreases, anaerobic SRB flourish and mixed biofilms are formed which leads to more aggressive MIC [5]. Titanium has been selected as the

condenser tube material for Prototype fast breeder reactor which is being built at Kalpakkam, Tamilnadu, India. Titanium possesses outstanding corrosion resistance in a wide range of aggressive environments [6]. The reason for the remarkable corrosion resistance of this material is the presence of inert, strongly adherent surface oxide film which forms almost instantly on exposure to moisture, air and many sources of oxygen [7]. With all its technical superiority, titanium has proven to be the choice of heat exchanger material for sea water cooled power plants. However, the inertness of titanium surface and its excellent biocompatibility makes it highly susceptible to biofouling [8]. Not much information is available on the influence of heterogeneous biofilms consisting of aerobic MOB and anaerobic SRB on the passivity of Ti alloys. Earlier studies in the author's laboratory on year long biofouling studies of titanium in seawater have confirmed the presence of aerobic MOB and anaerobic SRB in biofilms [9]. Recently, Rao et al., has reported that titanium becomes susceptible to pitting corrosion by freshwater anaerobic SRB *Desulfovibrio* sp. [10]. The main objective of this work is to study the influence of a consortium of anaerobic and aerobic bacterial biofilms and pure anaerobic bacterial biofilms on the localized corrosion resistance of titanium in natural seawater. Cyclic potentiodynamic polarization experiments were done for establishing localized corrosion resistance and surface characterization were used for characterizing the passive film before and after forming biofilm.

JCSE The Journal of Corrosion Science and Engineering
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# Experimental

## Material

The material used in this investigation is commercially pure (CP) Titanium (Ti) (ASTM Grade 2). The chemical composition of the material is presented in Table 1.

| Elements | Fe | O | N | C | Ti |
|---|---|---|---|---|---|
| Weight % | <0.3 | 0.25 | 0.03 | 0.1 | Balance |

Table 1. Chemical composition of CP Grade 2 Titanium

## Specimen preparation

Ti specimens with two different dimensions were used in the study as given below.

(i) Ti specimens with dimensions (20 x 15 x 1.6 mm) were ground with 80 to 1200 grit SiC paper. After grinding, the specimens were cleaned ultrasonically first with soap solution followed by distilled water and air-dried. These specimens were used in biofilms exposure studies, X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) analysis.

(ii) Ti specimens with dimensions (10 mm x 10 mm x 1.6 mm) were mounted in epoxy resin (araldite) with a brass rod for electrical connection. The details are described elsewhere

[11]. This mounted specimen with an exposed area of 1 $cm^2$ was ground to 1200 grit and was used for biofilm formation and for carrying out electrochemical cyclic potentiodynamic and cathodic polarization experiments.

## Development of biofilm on Titanium specimens

### Isolation and characterization of microbes

SRB was isolated from Titanium coupons exposed to sea water for two weeks in the pumping station of Nuclear Desalination Demonstration Plant located at Kalpakkam, India. Isolation and biochemical characterization of SRB was done as described in Bergey's Manual of Determinative Bacteriology [12]. The Postgate B medium used for isolation contains 10 g Tryptone, 1 g $Na_2SO_4$, 1 g $Na_2SO_3$, 2.5 g NaCl and 0.5 g Ferric Citrate in one liter of distilled water.

Manganese oxidizing bacterium (MOB) was isolated from surfaces of steel scraps in Indira Gandhi Centre for Atomic Research (IGCAR) storage yard and identified as *B. flexus* in the authors' laboratory [13], and the same was used in the present study.

### Molecular identification and phylogenetic analysis of isolated SRB

Genomic DNA of the bacterial isolate and amplification of gene encoding small subunit ribosomal RNA was carried out as described elsewhere [14]. The amplified product was purified using GFX™ PCR DNA and Gel Band Purification kit (Amersham Biosciences)

and cloned in pTZ57R/T vector according to the manufacturer's instruction (InsT/Aclone™ PCR Product Cloning Kit, MBI Fermentas), and transformants were selected on Luria Bertani medium containing ampicillin (100 µg/ml) and X-gal (80 µg/ml). DNA sequencing was carried out using ABI PRISM 310 Genetic Analyzer (PE Applied Biosystems). For sequencing reaction, Big Dye Ready Reaction DyeDeoxy Terminator Cycle Sequencing kit (Perkin-Elmer) was used. The sequence obtained was analyzed for its close related sequences using NCBI-BLAST search version 2.2.20 [15] and tools of Ribosomal Database Project II Release 10 (http://rdp.cme.msu.edu) for taxonomic hierarchy of the sequences. Phylogenetic analysis was performed with multiple sequence alignments using CLUSTAL X2 [16] with a collection of taxonomically related sequences obtained from the National Center for Biotechnology Information (NCBI) Taxonomy Homepage (http://www.ncbi.nlm.nih.gov/Taxonomy/taxonomyhome.html/) and Ribosomal Database Project-II Release 10 (http://rdp.cme.msu.edu). Molecular Evolutionary Genetic Anlaysis (MEGA) version 4.1 program [17] was used to construct phylogenetic tree (neighbor-joining method) and similitude analysis was done with the common 16S rRNA gene regions. 1,000 bootstrap replications were carried out to validate internal branches [18]. MatGAT v. 2.01 software [19] was used to calculate the similitude percentages among sequences.

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

### Exposure studies in cultures

Ti specimens were exposed to two bacterial groups viz., anaerobic SRB and aerobic MOB *B. flexus.* Semi-continuous SRB culture was maintained by replacing 50 % culture with sterile Postgate Medium B (described above) for every four days on the basis of the SRB growth curve. Maintenance of semi-continuous MOB culture was done as described elsewhere [13]. Biofilms of various duration were formed on the test coupons of Ti by exposing for various durations (two weeks, eight weeks and 12 weeks) in various cultures (SRB and MOB) as follows:

(i) exposed to SRB for two weeks

(ii) exposed to SRB for eight weeks

(iii) exposed to SRB for 10 weeks and MOB for two weeks

The SRB and MOB cells present in the biofilms on the exposed specimens were recultured in respective media and their presence and viability were confirmed.

## Post exposure characterization of biofilms and Titanium surfaces

### Microscopic observation of biofilms

Heterogeneous biofilm of SRB and MOB cells on Ti specimens were stained with 0.1 % Acridine orange stain and examined using Epifluorescence microscope (Nikon E600) for

confirming the presence of bacterial groups. Detailed methodology is described elsewhere [9].

Biofilmed Ti specimens were cleaned with sterile water to remove all loose biofilm. The specimens were fixed with 0.25 % Glutaraldehyde at 16°C overnight and then dehydrated with a series of ethanol-water combinations (20 % to 100 %) and then kept in vacuum desiccators. The surface morphological characteristics of the specimens were observed under scanning electron microscope (SEM) (XL30ESEM M/s Philips) at magnification ranging from 100X to 10000X operated at accelerating voltage of 15-30 kV.

### XRD analysis of the corrosion products

Ti coupons exposed to 12 week old heterogeneous biofilms were dried and the XRD pattern of the biofilm was recorded using computer controlled XRD-system (PanAnalytical Xpert) with Cu-Kα radiation (Ni filtered = 13418 A°) at the range of 40kV, 20A. The 'peak search' and 'search match' program built in software (syn master 7935) was used to identify the peak table and ultimately for the identification of XRD peaks.

### XPS analysis

XPS analysis was carried out on unexposed Ti (control) and Ti exposed to heterogeneous biofilm for 12 weeks to understand the influence of biofilm on passive layer of titanium. Ti specimens exposed to bacterial cultures were cleaned in sonicator bath with

absolute ethanol for removing all traces of biofilm and surface analysis of the specimens was carried out. Measurements were carried out by X-ray Photoelectron Spectrometer (SPECS make, Germany) using Al Kα line of the X-ray source at 1486.74eV. The anode was operated at a voltage of 13 kV and source power level at 300 W. Sputter-etch cleaning of specimens was done for 1, 3 and 5 minutes using an Ar ion source operated at 5 kV and 50 μA. Spectra were collected using the PHOIBOS 150 MCD-9 analyzer with a resolution of 0.67 eV for 656 kcps at pass energy of 10 eV.

## Cyclic potentiodynamic polarization studies of Ti covered with bacterial biofilms

Cyclic potentiodynamic polarization experiments were carried out in sea water as per ASTM standard G61-86 [20] on (i) freshly polished specimens (without any biofilms) and (ii) specimens with two weeks and eight weeks old SRB biofilms and (iii) specimens with heterogeneous biofilm of 10 week exposure in SRB culture followed by two weeks exposure in MOB culture. A computer controlled potentiostat (AUTOLAB PG60, Netherlands) was used to conduct the cyclic potentiodynamic polarization experiments. A three-electrode electrochemical cell was used consisting of test coupon as the working electrode, saturated calomel electrode (SCE) as the reference and a platinum foil as the auxiliary electrode. Sea water from Kalpakkam coast (salinity – 35 ppt, chloride – 18,981 ppm, sulfate – 2650 ppm, pH – 8.1) [21] was used as the electrolyte. Open circuit potential (OCP) was measured after

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

exposing the specimens to the test solution for 10 minutes. Cyclic potentiodynamic polarization was carried out by scanning the electrode potential from OCP anodically at a scan rate of 10 mV/min up to 1000 mV(SCE) and reversing the scan direction. For all experiments, electrode potential Vs current plots were recorded. After every cyclic polarization experiments, the specimens were cleaned ultrasonically and air dried and examined under Leica make Optical microscope for evaluating the nature of corrosion attack.

### Potentiodynamic cathodic polarization studies

In order to understand the influence of 2 week SRB biofilm on the cathodic polarization behavior of CP Ti, cathodic polarization experiments were carried out from OCP to -1200 mV(SCE) at a scan rate of 10 mV/min for the material with and without SRB biofilm.

## Results and Discussion

### Characterization of microbes and Biofilms on Titanium

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

The morphological and biochemical characteristics of SRB isolate revealed that it was Gram negative vibrio shaped, non-sporulating, $H_2S$ producing, lactate utilizing *Desulfovibrio* sp. The 16S rRNA sequencing and phylogenetic analysis (Fig. 1) confirmed that the SRB isolate as *Desulfovibrio ferrophilus*, having 99.6 % similarity with *D. ferrophilus* of Genbank (AY274449). The 16S rRNA gene sequence of the *D. ferrophilus* of the present study has been submitted to Genbank under accession number JQ742965.

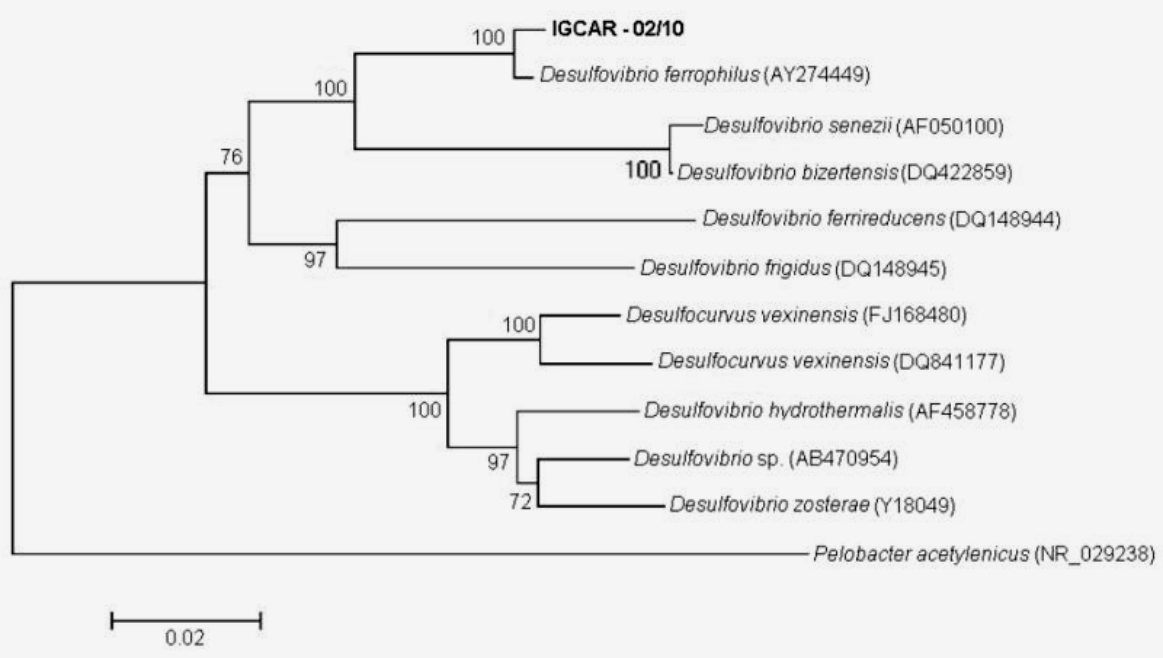



Fig.1. Neighbor-joining tree based on 16S rRNA gene sequences, showing phylogenetic relationships between *Desulfovibrio* related sequences. *Pelobacter acetylenicus* was used as the out-group sequence. Numbers at nodes indicate bootstrap values >50% from 1,000 replicates. GenBank accession numbers are given in parentheses. The scale bar indicates sequence divergence

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

Fig. 2 (a) presents the epifluorescence micrograph of the microbial cell of rod shaped *Bacillus flexus* and Fig. 2 (b) presents that of vibriod shaped *Desulfovibrio* sp. from the bacterial cultures streaked on glass slides and stained with acridine orange. The distinct morphology of the two bacterial species is clearly brought out in these figures.

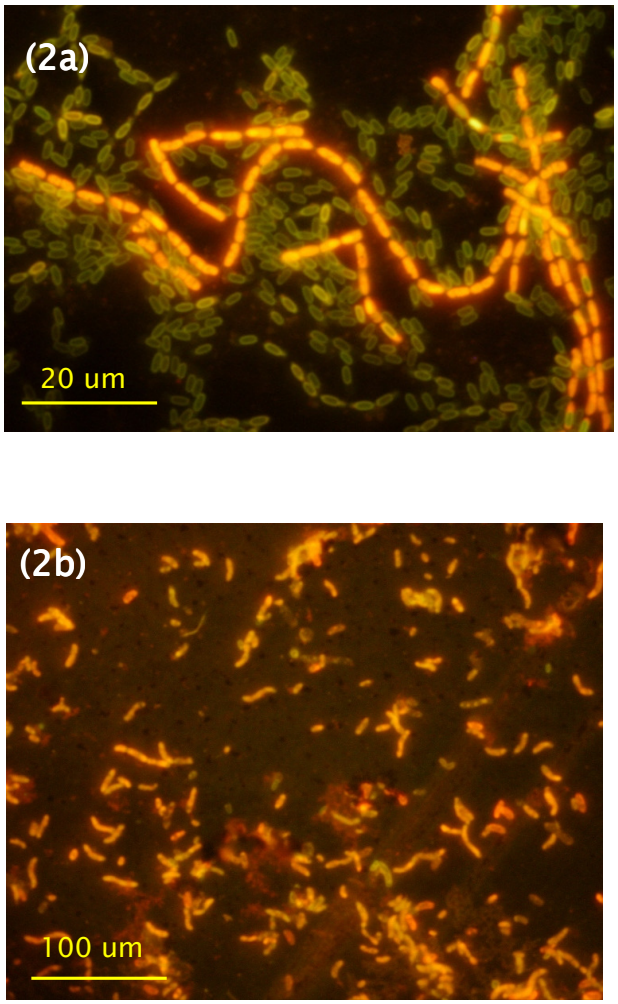
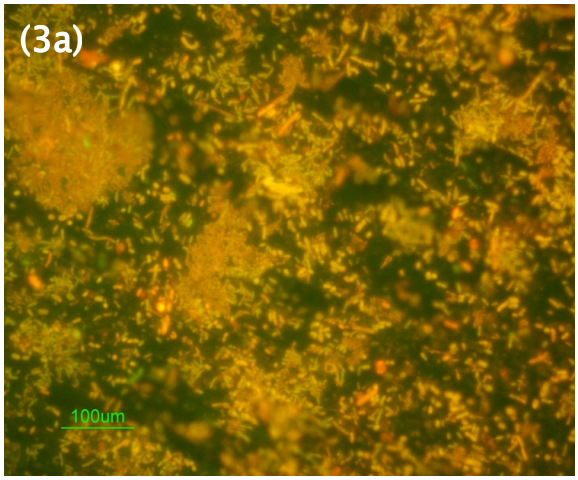
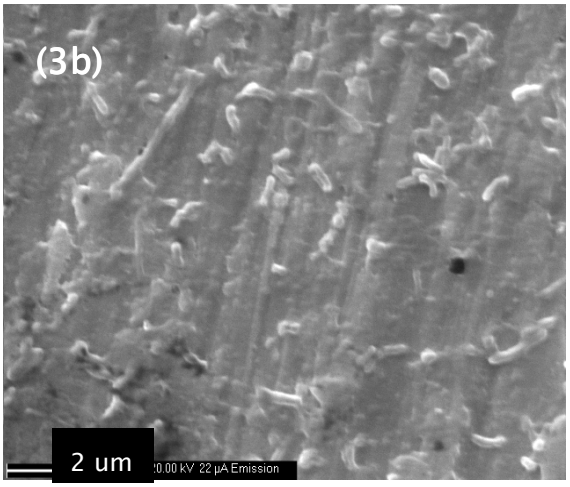



Fig. 2 Epifluorescence micrographs of (a) rod shaped sporulating MOB *B.flexus* and (b) vibrio shaped SRB *Desulfovibrio ferrophilus*

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

SEM micrographs and epifluorescence micrographs of heterogeneous biofilm of SRB with MOB on Ti specimens are presented in Figs. 3. Microbial cells with dense orange fluorescence of RNA could be observed in epifluorescence micrographs (Fig. 3a). SEM micrographs (Fig. 3b) distinctly showed the presence of vibrioid shaped SRB *D. ferrophilus* and rod shaped MOB *B. flexus on* Ti.



JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

Fig. 3 (a) Epifluorescence micrographs of heterogeneous biofilm on titanium showing the fluorescing SRB and MOB cells, and (b) SEM micrograph of mixed biofilm on titanium distinctly showing vibrio shaped SRB and rod shaped MOB cells

## XRD analysis

The XRD pattern obtained for Ti specimen exposed to heterogeneous biofilm is presented in Fig. 4. From these data it can be inferred that these compounds namely FeO(OH), $Fe_2O_3$, FeS, $Fe(OH)_2$ and hydrated $Fe(OH)_3$ are present on Ti specimen with 12 weeks mixed biofilm. *Desulfovibrio ferrophilus* is reported [22] to be capable of reducing sulfate and ferric ions in the growth media leading to the formation of these compounds.

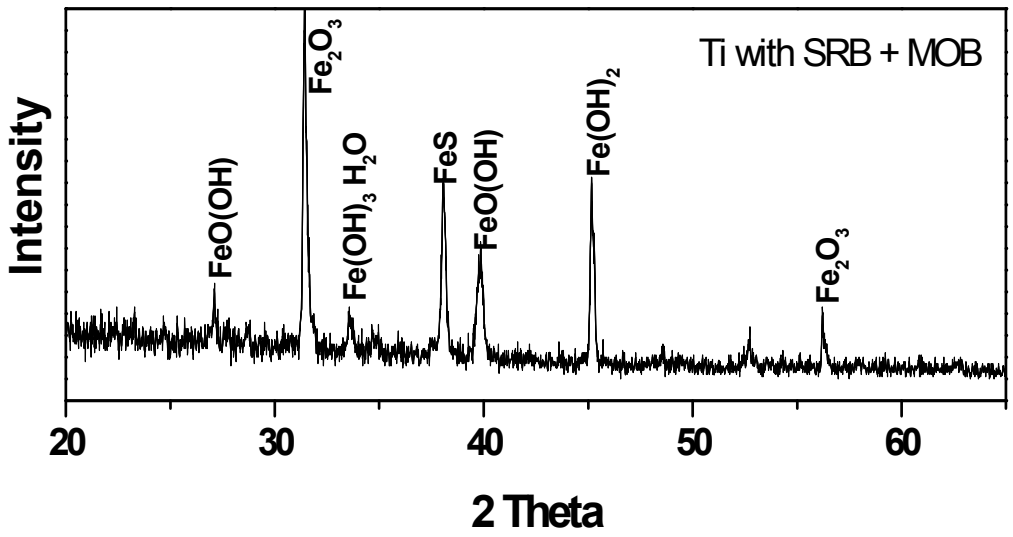
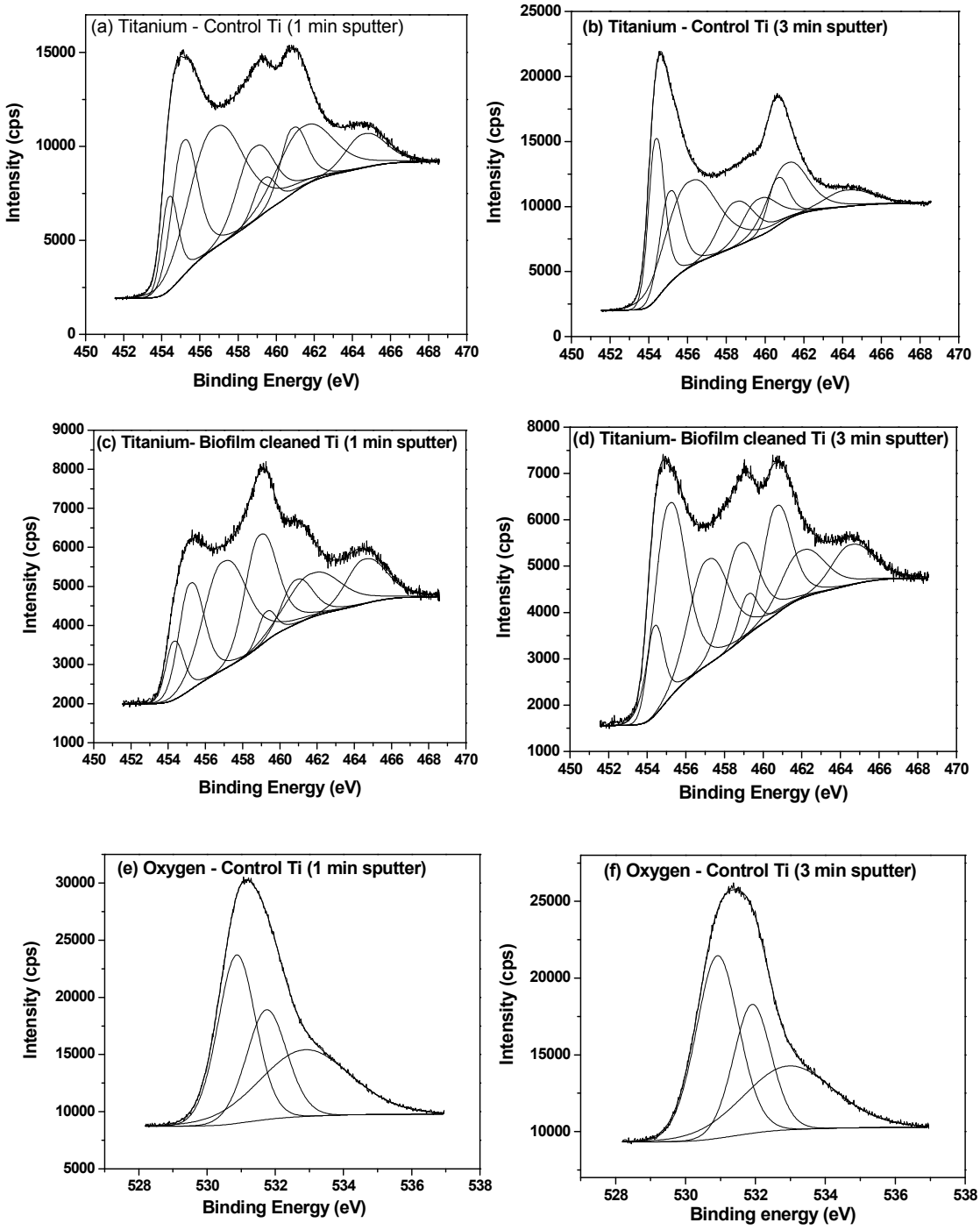



Fig. 4 X-Ray Diffractogram for Ti with heterogeneous (SRB and MOB) biofilm

## XPS analysis

XPS spectra of the passive film of Ti samples are shown in Figs. 5a to 5l representing the presence of metallic and oxidized Ti peaks and spectra for the passive film of Ti specimen exposed to mixed biofilm. The presence of metallic and oxidized Ti peaks was seen in these Ti specimens (Figs. 5a to 5d). XPS analysis of the passive films of control Ti and bio-film grown Ti samples, sputtered for 1 min and 3 min, reveal that the films are different. The control Ti sample shows that the passive film is $TiO_2$ and with sputtering, lower oxides of Ti are revealed due to the preferential sputtering of Oxygen. This is seen from de-convolution of the high resolution spectra of 2p core level of Ti (Figs. 5a-5d) and 1s core level of O (Figs. 5e-5h). The 2p region of Ti shows the doublet structure of 2p3/2 and 2p1/2 regions distinctly. The de-convolution shows four doublets. The doublet at 454.3 eV & 459.7 eV suggest metallic Ti state, at 455.1 eV and 460.5 eV suggest Ti (+2) state, at 456.4eV and 461.9 eV suggest Ti (+3) state and at 458.9 eV and 464.5 eV suggest Ti (+4) state. The de-convoluted 1s region of O shows three peaks at 530.5 eV, 531.5 eV and 533.0 eV indicating the O-Ti, -OH and adsorbed $H_2O$ respectively. Similarly, the bio-film grown Ti sample shows that the passive film is modified slightly that can be seen from the presence of Fe and S along with Ti and O. Within the binding energy range from 705 to 740 eV the presence of $Fe^{2+}$ peaks (Figs. 5i and 5j) and within the binding energy range from 160 to 166 eV the presence of $S^{2-}$ peaks (Figs. 5k and 5l) was seen on this surface

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013



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ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

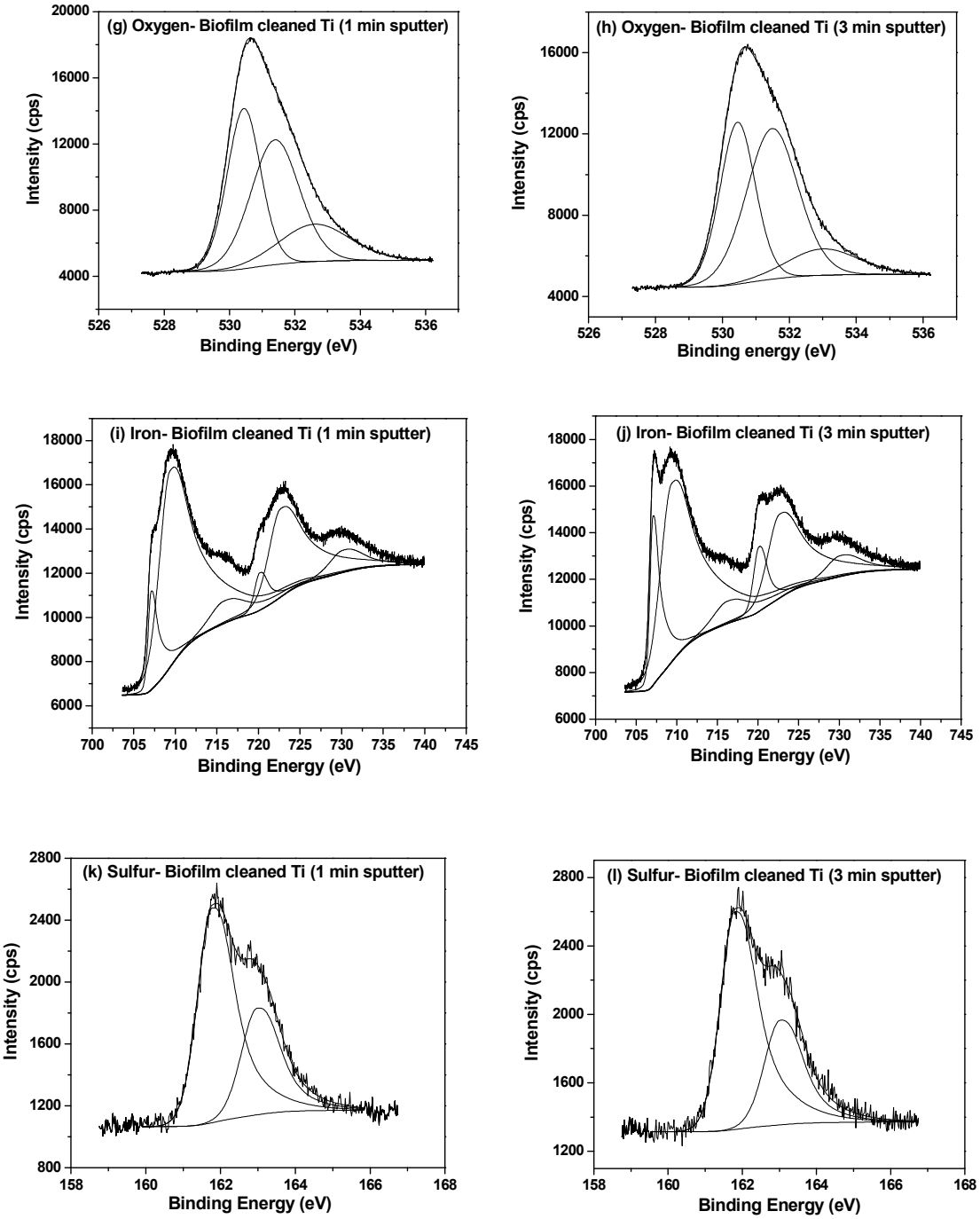



Fig. 5 XPS analysis of Titanium on Control Ti and biofilm cleaned Ti – 1 and 3 minute sputtered with Argon (a to d); Oxygen on Control Ti and biofilm cleaned Ti 1 and 3 minute

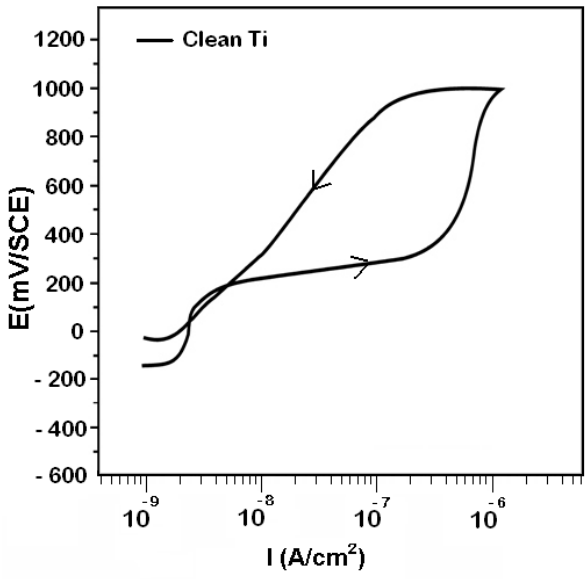
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

sputtered with Argon (e to h); Iron on biofilm cleaned Ti (i and j); Sulfur on biofilm cleaned Ti (k and l)

even after sputter etch cleaning for 5 minutes. Fe is found to be in +2 oxidation state where as S is as FeS. This is seen from the de-convolution of the 2p core levels of the Fe and S. The 2p region of Fe shows the distinct doublet structure. The de-convolution shows three doublets. The doublet at 707.1 eV and 720.1 eV suggest metallic Fe, at 709.4 eV and 722.6 eV suggest Fe (+2) state and at 716.0 eV and 730.2 eV suggest the satellite peak structure of Fe (+2) state. The de-convolution of the 2p region of S shows a single doublet at 161.8 eV and 163.0 eV indicating FeS. With sputtering, the concentration of higher oxidation states of both Fe and Ti reduce and the metallic states increase.

## Cyclic potentiodynamic polarization studies

Cyclic potentiodynamic polarization curves obtained for clean Ti and Ti under biofilms of SRB and MOB are given in Fig. 6 (a) and 6 (b).



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ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

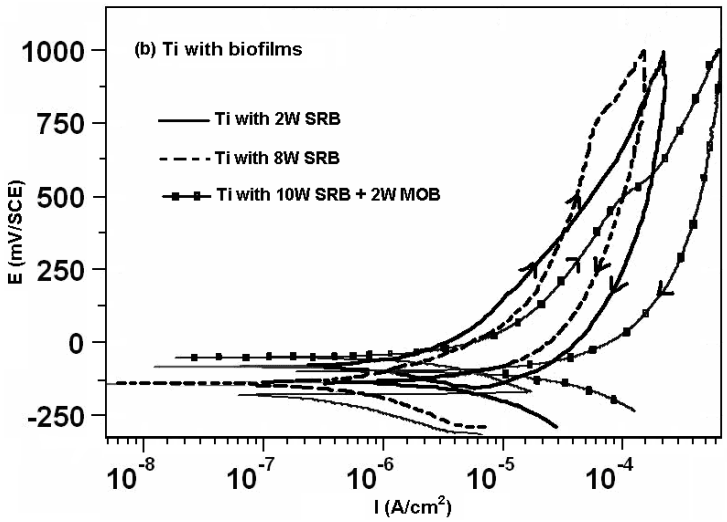


Fig. 6 Cyclic anodic potentiodynamic polarization curves for (a) clean Ti and (b) Ti specimens with SRB and mixed biofilms (SRB and MOB) in seawater

Electrochemical parameters viz. OCP, breakdown potential, repassivation potential and passive current density were measured from these curves and are presented in the Table 2.

| S.No | Type of biofilm/exposure period | OCP mV(SCE) | $E_b$ mV(SCE) | $E_{repass}$ mV(SCE) | $i_{pass}$ μA cm$^{-2}$ |
|---|---|---|---|---|---|
| 1. | Freshly polished unexposed (no biofilm) | – 180 | – | – | 0.8 |
| 2. | With 2W SRB | – 80 | – | – | 8.0 – 10.0 |
| 3. | With 8W SRB | – 40 | + 740 | – | 14.0 – 80.0 |
| 4. | With 10W SRB + 2W MOB | – 20 | + 480 | –25 | 22.0 – 100.0 |

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

Table 2. Electrochemical parameters observed from anodic polarization curves with Ti specimens exposed to SRB and MOB biofilms

Cyclic polarization curves of freshly polished clean Ti showed very low passive current (0.8 μA $cm^{-2}$) and negative hysterisis [23] implicating the passivity of Ti and absence of any localized corrosion. Two week old SRB biofilm on Ti increased the passive current to >10 μA $cm^{-2}$ with positive hysterisis showing the initiation of localized corrosion activity. Eight week old SRB biofilm caused one fold increase of passive current density (20 to 80 μA $cm^{-2}$) and 12 week old heterogeneous biofilm of SRB and MOB caused two fold increase of passive current density (40 to 100 μA $cm^{-2}$).

After the cyclic polarization experiments, the specimens were examined under optical microscope. The clean Ti did not undergo any localized attack and hence no break down potential can be seen from the cyclic polarization curve. However, 8 weeks old SRB and 12 weeks old mixed biofilm resulted in breakdown of passive film at +740 mV(SCE) and +480 mV(SCE) respectively. Pitting attack can be seen as presented in Fig. 7.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

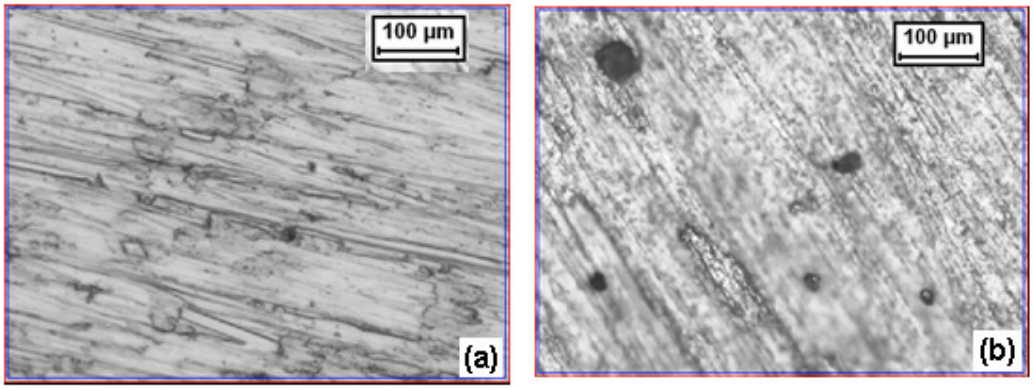


Fig. 7. Optical Micrographs of anodically polarized Titanium specimens in seawater (a) Control Ti, (b) Ti with heterogeneous biofilm (arrow indicating localized attack)

## Cathodic Potentiodynamic Polarization Curves

Cathodic potentiodynamic polarization curves (Fig. 8) showed one order magnitude of increased cathodic current on Ti with 2 week SRB biofilm ($10^{-4}$ A $cm^{-2}$) compared to clean Ti ($10^{-5}$ A $cm^{-2}$).

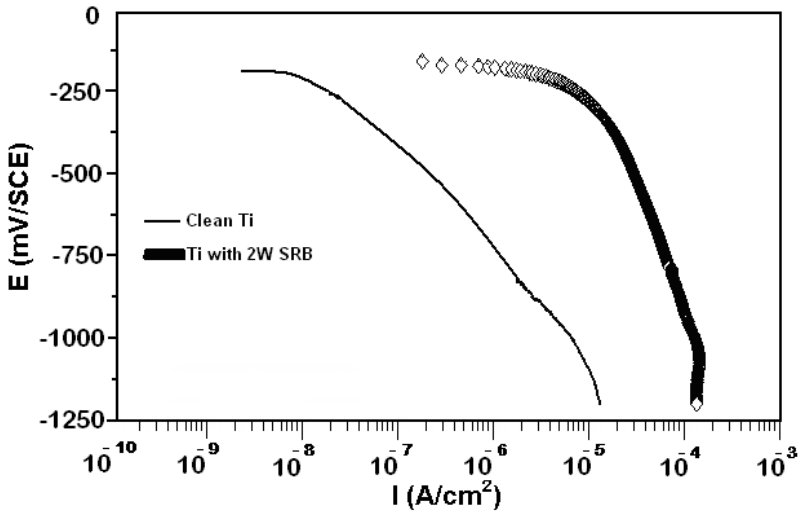


Fig. 8. Cathodic polarization curve for Ti specimens with 2 week SRB biofilm in seawater

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

*D. ferrophilus* isolated and identified in this present study have been so far reported only in the corrosion of iron [24]. Aerobic biofilms of MOB are reported to cause ennoblement of materials due to manganese deposition [25, 26]. MOB isolate *B. flexus* used in this study was also reported in corroding SS304 material [13]. However, this is the first study on corrosion on titanium by a mixed biofilm of anaerobic SRB isolate *D. ferrophilus* and aerobic MOB isolate *B. flexus*.

SRB strains require strict anaerobic condition [27] for growth and hence the titanium with 2 weeks and 8 weeks patchy biofilms of SRB (Fig. 4a) has oxygen concentration cells. Due to non-availability of oxygen for $TiO_2$ maintenance, thinning of passive film can happen and the XPS results have shown reduction in intensity of titanium and oxygen peaks under biofilms. Pouilleau et al [28] reported that the passive films composed of an amorphous $TiO_2$ outer layer (10-20 nm thick) and an intermediate TiOx layer, in contact with the $TiO_2$ layer and the metallic substrate. According to these workers, this outer layer is sensitive to environment and its thickness decreases in corrosive environments. The XPS results have confirmed this under SRB biofilms in the present study. For anaerobic respiration SRB use sulphate as terminal electron acceptor and the reduction of the same with hydrogen result in sulphide production [29]. In metal interphases utilization of hydrogen result in cathodic depolarization that can enhance cathodic current [30, 31].

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

Cathodic polarization curves on titanium with two week SRB biofilm clearly showed enhanced cathodic current that may be due to electron transfer mechanism from metallic surfaces. The same observation has also been discussed by Cordas et al [27] on the enhanced hydrogen reduction reaction obtained with the SRB biofilms formed in polarized SS surfaces. They observed that the electrodes polarization seems to have a selective effect on the electro catalytic enhancement, with the observation of higher currents towards the hydrogen reduction due to SRB metabolism. The presence of sulfide in biofilms on titanium was confirmed by XRD patterns in the present study. XRD patterns of biofilms on titanium also showed the presence of FeS. The source of ferrous ions is the bacterial medium. Hang [22] has studied this species of *D. ferrophilus* in detail and reported that they can also reduce ferric ions (Ferric citrate in the bacterial medium), hence the name *D. ferrophilus* was proposed. These ferrous ions react with sulfide and form ferrous sulfide. They can also form FeO(OH), $Fe_2O_3$, $Fe(OH)_2$ as confirmed by XRD analysis of biofilm. Cyclic potentiodynamic curves showed increased passive current and positive hysterisis for Ti specimens with 2 week and 8 week SRB biofilm indicating localized corrosion initiation by the action of SRB alone on the passive film. According to Moon et al [32] pitting corrosion occurs under SRB biofilm by accelerated cathodic reaction and oxygen concentration cell.

The 12 weeks heterogeneous biofilm on titanium is comprised of 10 weeks SRB biofilm and 2 weeks MOB biofilm. XPS analysis of the surface showing presence of $Ti^{4+}$, $Fe^{2+}$ and $S^{2-}$ peaks in the passive films of cleaned biofilmed surface and even after sputter etch cleaning for 5 minutes suggest the modification of the passive film due to biofilm activity even before polarization. Sulfide ions could have interacted directly with the porous $TiO_2$ passive film and helped the entry of $Fe^{2+}$ ions also. From the cyclic potentiodynamic curves of titanium covered with heterogeneous biofilms, it can be seen that the passive current was varying between 22 to 100 μA $cm^{-2}$. This is much higher than that observed for 2 weeks and 8 weeks biofilms of SRB. This implies that the localized corrosion attack of titanium covered with heterogeneous biofilm is more severe than that of homogeneous 2 weeks and 8 weeks SRB biofilm. Optical microscopic observation confirmed localized corrosion and pits on Ti. On the surface of the specimens covered with heterogeneous biofilms there is a combination of the oxygen reduction step by aerobic *B. flexus* in addition to sulfide metabolism by anaerobic SRB. Biomineralization of manganese oxide by *B. flexus* is already confirmed in authors' earlier studies [13]. This biomineralization of manganese oxide on the titanium surface by MOB can cause ennoblement with aerobic biofilmed areas which in turn create better cathodes. These cathodes accelerate corrosion in the anodic areas covered with anaerobic SRB biofilms. Thus heterogeneous biofilms provided better galvanic couplings that led to increased localized corrosion of titanium.

ISSN 1466-8858 Volume 16, Paper 26 submitted 14 June 2013

Schematic representation of localized attack of titanium covered with SRB biofilms by thinning of passive films and when covered with mixed biofilms of SRB and MOB by galvanic coupling is shown in Fig. 9.

## Conclusions

The influence of a consortium of anaerobic and aerobic bacterial biofilms and pure anaerobic bacterial biofilms on the localized corrosion resistance of titanium in natural seawater is studied in this investigation. Exposure of titanium covered with bacterial biofilm to seawater resulted in pitting corrosion. The severity of localized attack increased with increase in the age of the biofilm. From the XRD and XPS investigations, it was inferred that anaerobic biofilms of SRB has created oxygen depleted areas where sulphate reduction by SRB led to sulphide ion formation which caused thinning of passive film and pitting attack.

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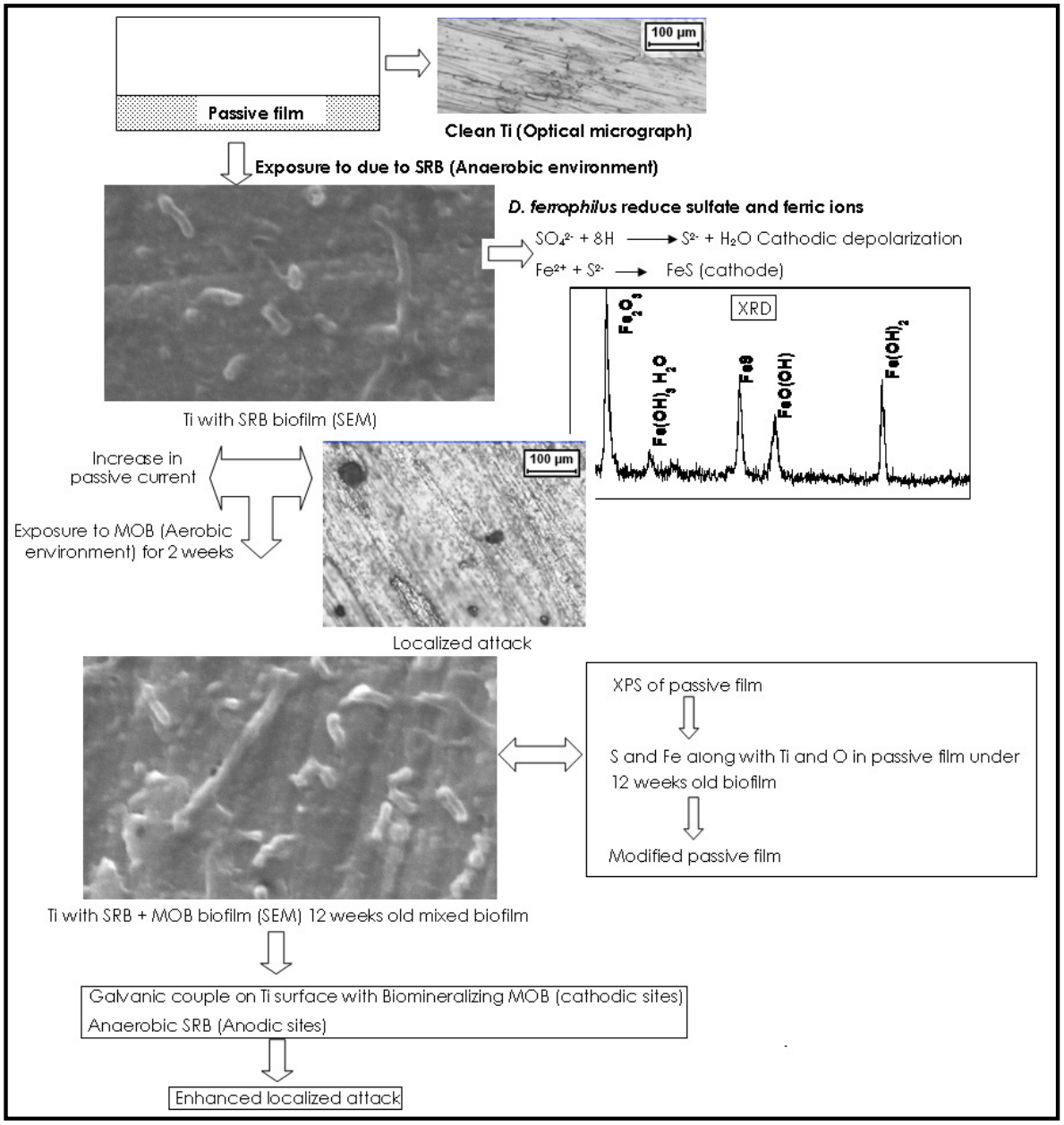


Fig. 9. Schematic representation of localized attack of Ti under SRB and heterogeneous biofilms of SRB and MOB

In the case of heterogeneous biofilm, MOBs can create additional cathodes due to biomineralisation of Mn and SRBs can create local anodes under the oxygen depleted condition. Thus heterogeneous biofilms provided more severe galvanic coupling which leads to severe pitting attack. From this investigation it is established that although titanium possess excellent localized corrosion resistance in seawater, bacterial biofilms can breakdown the passive film leading to localized corrosion.

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