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A state-of-the-art review on passivation and biofouling of Ti and its alloys in marine environments

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ABSTRACT

High strength-to-weight ratio, commendable biocompatibility and excellent corrosion resistance make Ti alloys widely applicable in aerospace, medical and marine industries. However, these alloys suffer from serious biofouling, and may become vulnerable to corrosion attack under some extreme marine conditions. The passivating and biofouling performance of Ti alloys can be attributed to their compact, stable and protective films. This paper comprehensively reviews the passivating and biofouling behavior, as well as their mechanisms, for typical Ti alloys in various marine environments. This review aims to help extend applications of Ti alloys in extremely harsh marine conditions.

1. Introduction

Ti alloys have been identified as superior corrosion-resistant lightweight structural materials in aerospace applications. These materials can also reduce the weight of components in transport applications and thus the consumption of fuel [1–3]. For example, Ti alloys can be made into connecting rods, valves, wheel rim screws and suspension springs for racing cars [4], and used for tail covers and turbine blades in aircraft engines [2]. Because of their excellent corrosion resistance, they are even commonly used as permanent orthopedic and dental implants [5,6].

The excellent mechanical strength and chemical stability of Ti alloys along with the opportunity for weight reduction make these materials ideal for seawater related engineering applications. For example, they have been made into fasteners in marine industry, hydrocarbon extraction devices in offshore petrol-chemical industry, heat exchangers in desalination plants, and cooling systems in seawater-cooled power plants [7–9]. Many researchers [10–13] have compared the corrosion rates of Ti alloys with those of other metallic materials in marine environments, and found that the measurement and evaluation of short-term corrosion damage of Ti alloys are relatively difficult due to their high corrosion resistance.

However, Ti has a serious biofouling problem because of its excellent biocompatibility. In marine engineering, biofouling is an issue as critical as corrosion damage. Most investigators are particularly interested in the adherence mechanism of bacteria on Ti in seawater and the corresponding antifouling strategies [14–17], but they often ignored the effect of the surface conditions or state of Ti on biofouling in seawater.

It is true that Ti and its alloys are highly corrosion resistant in general environments. Yet in certain service conditions, failure of Ti components does occasionally occur. For example, the bond interfaces of heat exchangers made of grade 3 Ti were deformed and eventually destroyed by hydride in seawater [18]. Similarly, tubes made of grade 2 Ti, exposed to a natural seawater environment within heat exchangers, ruptured due to hydrogen assisted corrosion (HAC) [19]. Even worse, corrosion and biofouling may occur

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concurrently. Ti per se can have a biofouling load about 0.56 g/cm^2 in field [20]. Simultaneous corrosion would definitely multiply this damage. It was reported that a large size of perforation occurred in a Ti condenser tube, which was suffering serious fouling in a seawater environment, as a result of the erosion-corrosion caused by turbulent flow in the biofouling area [21].

In nature, corrosion and biofouling could be correlated, as they are both closely associated with the surface state or film of a Ti alloy. However, many investigators simply looked at them separately. So far, corrosion/passivity and biofouling of Ti alloys have never been reviewed together, and the passivating and biofouling performance of Ti alloys in emerging marine applications have not been comprehensively summarized.

This review paper provides a brief description of the physical-chemical properties of Ti alloys before describing the primary mechanisms governing the growth of oxide films on Ti surfaces. Following that, the paper further summarizes various types of corrosion damage in marine environments, describes microbiologically influenced corrosion (MIC) and microbiologically influenced corrosion inhibition (MICI) phenomena, and lists some anticorrosion and antifouling strategies adopted in the field. The purpose of this review is to identify current research gaps and potential breakthrough areas for Ti alloys for future marine engineering applications.

2. Basic physical and chemical properties

Excellent corrosion resistance and biocompatibility are two of the most outstanding features of Ti and its alloys. Ti is more corrosion resistant than aluminum, stainless steel and brass [22,23]. The crevice corrosion of grade 2 Ti in seawater is negligible at temperatures up to 80 °C [24]. Addition of Pd can increase the crevice and pitting corrosion resistance of grade 7 and grade 11 alloys, allowing them to be used in reducing acid environments [25]. Because of its excellent biocompatibility, Ti is one of the most popular implant materials, and has been widely used in clinical applications. For example, the adhesion of tissue and ingrowth of orthopedic and dental implants can be improved if Ti and its alloys are used [5,26–28]. It has been reported that the commendable biocompatibility of Ti implants generally comes along with good *in vivo* bacterial adherence, which could result in failure of transplant operations [29–32].

The high corrosion resistance of Ti is attributed to the compact and stable oxide film spontaneously formed on its surface in air or in oxygen containing environments. Thermodynamically, pure Ti is reactive having a standard electrode potential as negative as −1.63 V_{SHE} [33]. Its surface is normally covered by a passive film, which is intact in most ordinary conditions and can effectively separate Ti from environmental medium. Once the film breaks down, it can be rapidly repaired in the broken area. Rapid corrosion may occur once its protective film decomposes under an anaerobic environment. Ti is not completely immune to corrosion in acid media (see Fig. 1) [34], especially in reducing acidic solutions. It has been reported that pitting corrosion can occur in solutions containing F^- or Br^-, and some organic solutions like formic acid (and formates) in certain conditions [35–38]. In fairly strong oxidizing media of dry chlorine and fuming nitric acid, Ti can also react fiercely as its oxide film is not stable in this case [39]. To improve fatigue resistance and wear resistance, β phase stabilizers are sometimes added into Ti [40]. In developing new biocompatible Ti alloys, toxicity and modulus should be carefully specified in addition to passivity [41,42].

Since many physicochemical properties of a Ti alloy are determined by its surface passive film, it is most likely that this film also critically determines the passivating and biofouling behavior.

3. Oxide films

3.1. Native oxide film

The high corrosion resistance of Ti can be attributed to its surface oxide film. Such a corrosion resistant film on Ti is a thin oxide layer spontaneously formed on the surface in atmosphere or an aqueous solution, or obtained through a special process, such as anodic oxidation or hydrothermal treatment. From a thermodynamic point of view, Ti can rapidly react with oxygen and produce stable Ti oxides. The air-formed incipient film, *ca.* 1 ~ 8 nm thick, is primarily composed of amorphous TiO_2 with a band gap energy of 3.05 eV [37,43,44], which can be affected by the ambient environment to a certain extent [43,45–47]. The reaction equation can be expressed as follow [37]:

$$Ti + O_2 = TiO_2 \quad (1)$$

Thickness of the oxide film exposed in the air increases with time. Chan et al. [48] reported that a chemisorbed amorphous film was formed on the transition metal surface along with oxygen adsorption.

3.2. Passivation models

To better reveal passivating mechanism, many models have been proposed [49–52], among which the point defect model (PDM) based on migration of anion vacancies appears a reasonable and widely accepted one. It has been used to interpret stationary passivation [53]. Many modified PDMs have also been reported. For example, a combination of PDM with Wagner's theory [54] was proposed for Ti in acid solutions [55]. Seyeux et al. [56] came up with a generalized model on the basis of PDM by introducing a potential modification. This model can describe non-stationary oxide growth in aqueous solution. "High-field point defect" model was recently proposed to further optimize PDM. In this model, a decrease in electric field can mitigate the transport of charged lattice vacancies with increasing film thickness [57]. Different from PDM, a high field model (HFM), Mott-Cabrera model, has also been proposed based on migration of interstitial cations under non-stationary conditions [58]. The thickness of the oxide film according to HFM can be infinite if the applied voltage is high enough, which is unreasonable. Considering the semi-conduction of charge carriers and the transportation of anions and cations, Song proposed a passivation-transpassivation-second passivation model for 304 stainless steel [51], which successfully explained the increase in film thickness and EIS changes with increasing potential in the passive, transpassive and secondly-passive regions. For Ti at high anodic potential region, the current density peak may also be predicted by this model.

Experimental data have showed that PDM is more appropriate for Zr, W, Ta etc. than HFM [52]. It may also be applicable for Ti, as the oxide film on Ti is a multi-layer on Ti, which cannot be described by HFM. However, according to the newly developed PDM, film resistance should be dominated by a porous outer layer [53,59]. This inference is contrary to the Ti oxide structure. Therefore, more investigations may still be needed in order to establish a more comprehensive film model for Ti [53].

3.3. Potential dependent oxide film

Anodic oxidation can effectively grow a film on Ti, and has become one of the most prevalent, simple and low-cost electrochemical treatments [60]. The applied anodization potential mainly drops across the oxide film. The high electric field derived from the potential drop impels the migration of Ti^{4+} and O^{2-} ions to form TiO_2 and accelerates the growth of the oxide film [60]. Delplancke

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