Abstract

Metallic alloys with excellent structural and chemical properties play a significant role in a variety of applications. The selection of suitable metallic materials for marine gas turbine engine components is a real challenge as the surrounding environment is highly corrosive and the components have to function for a designed period at varied elevated temperatures. This chapter explains the selection of a suitable metallic alloy for marine gas turbine engine compressor section components based on extensive experimental data on two titanium-based alloys 6242 and IMI 834 under simulated marine gas turbine engine environmental conditions. The results revealed that 6242 exhibits superior performance over IMI 834. Therefore, the titanium alloy 6242 in association with appropriate protective coating is recommended to fabricate components intended to use for marine gas turbine engine compressor section applications.

Keywords: titanium alloys, marine gas turbine engines, hot corrosion, degradation mechanism, smart coatings

1. Introduction

Metallic alloys consist of one or more elements including small amounts of non-metals to improve their structural, corrosion, biomedical, magnetic properties, etc., which play a significant role in a variety of applications and environments. They are used extensively for commercial applications due to their cost-effective performance. Brass, bronze and various types of steels are the common metallic materials. However, selecting appropriate metallic materials for strategic applications such as defence, aerospace, and gas turbines of different types is a challenge. Excellent strength and lightweight properties made titanium-based alloys...
attractive candidate materials to fabricate components for aerospace applications. Enhanced strength of titanium alloys is obtained by solid solution alloying and stabilization of two-phase structures. The titanium alloys exhibit good corrosion resistance due to the formation of titania on their surface. However, the nature, composition and thickness of the protective oxide scales depend on the environmental conditions as well as nature and concentration of alloying elements. Due to the combined effects of elevated temperatures and exposure to harsh fuel and marine environmental conditions, hot corrosion has become a growing obstacle in meeting the desired efficiency of marine gas turbines. Therefore, it is essential to understand the corrosion characteristics of the titanium alloys under simulated marine engine environmental conditions [1].

Substantial amount of work was carried out by principal author and his co-workers on titanium-based alloys for their high-temperature oxidation and hot corrosion resistance in a variety of environments for aerospace applications, and the mechanisms under which they degrade were proposed [2–13]. He also developed an oxidation model to predict the life of titanium alloy components under gas turbine engine applications and demonstrated the validity of model with experimental data [14]. Furthermore, he successfully developed high-performance protective coatings for titanium alloy components for gas turbine engine applications [15–18]. Apart from aerospace applications, the utility of IMI 834 alloy for biomedical applications was also studied [19]. Recently, highly ordered titania nanotubes were successfully synthesized on different types of titanium alloys for a variety of applications including the solarization of a variety of systems starting from household to space vehicles and prevention of global warming, which is a major challenge for the world at present [20–23].

For obtaining higher efficiencies, the materials should satisfy both mechanical and corrosion resistance for industrial applications. It is pertinent to mention the fact that corrosion determines the life of components in a variety of industries. Therefore, material selection based on their corrosion resistance (if selected) enhances the efficiency, reduces down time, which in turn improves the production significantly and subsequently profitability [13]. In the present investigation, an attempt has been made to understand the properties of 6242 and IMI 834 and select a suitable alloy for fabrication of components used in marine gas turbine industries by carrying out a systematic corrosion study under marine gas turbine engine environmental conditions (hot corrosion) at different elevated temperatures.

2. Hot corrosion of titanium alloys

The chemical composition of selected titanium alloys is presented in Table 1.

2.1. Weight change measurements

Figure 1 shows the weight change as a function of exposure time for the titanium alloy IMI 834 in hot corrosion environment at three different temperatures. It can be observed that the weight change is increasing with exposure time and temperature. The degree of weight change at 700°C is significant compared with the remaining temperatures. After 40 h of exposure time,
the weight change becomes constant at 500 and 600°C. However, at 700°C, the weight change increases rapidly with time and reaches 16 mg/cm², which is about four and six times more when compared with 500 and 600°C, respectively. It indicates that higher temperatures are much severe for the alloy under hot corrosion conditions.

| Alloy  | Al  | Sn  | Zr  | Mo  | Nb  | Si  | C   | O   | Ti   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|------|
| IMI 834 | 5.8 | 4.06| 3.61| 0.54| 0.7 | 0.32| 0.5 | 0.105| Balance |
| Ti 6242 | 6   | 2   | 4   | 2   | -   | 0.1 | -   | -   | Balance |

Table 1. The chemical composition of selected titanium alloys (wt.%).

Figure 1. Weight change as a function of exposure time for IMI 834 at varied temperatures.

Figure 2. Weight change as a function of exposure time for Ti 6242 at varied temperatures.

**Figure 2** shows the weight change as a function of exposure time for the titanium alloy 6242 in hot corrosion environment at 500, 600 and 700°C. From the data, it can be observed that the weight change is increasing with exposure time and temperature. The weight change for the alloy at 700°C is increasing rapidly compared to lower temperatures, that is, 500 and 600°C. The weight change patterns are almost similar at 500 and 600°C and the change is only about 2 mg/cm². It is important to mention that unlike other alloy IMI 834, the weight change is less for 6242 at all the studied temperatures.
| Temperature (°C) | IMI 834     | 6242     |
|----------------|------------|----------|
| 500            | $1.68 \times 10^{-2}$ | $1.6 \times 10^{-4}$ |
| 600            | $1.81 \times 10^{-2}$ | $1.6 \times 10^{-3}$ |
| 700            | 6.5        | 1.52     |

*Table 2.* Rate constants of titanium alloys at different temperatures (mg2/cm4/h).

| Alloy       | Activation energy (KJ/mole) |
|-------------|-----------------------------|
| IMI 834     | -587.41                     |
| 6242        | -286.31                     |

*Table 3.* The activation energies of IMI 834 and 6242 alloys.

Based on the weight change data at different temperatures for both the alloys, the rate constants were evaluated and are presented in *Table 2*. The rate constant is almost twice for IMI 834 compared with 6242 at 500°C, one order more at 600°C and four times at 700°C. The activation energies evaluated for both the alloys are shown in *Table 3*. It is important to mention that the activation energy for IMI 834 is about twice as that of titanium alloy 6242, indicating that it is more reactive with the marine environment.

2.2. X-ray diffraction (XRD)

The XRD results revealed that the hot corrosion products for both the alloys studied at different temperatures are predominantly the oxides of titanium, aluminium and tin.

2.3. Scanning electron microscopy/electron dispersive X-ray spectroscopy (SEM/EDS)

*Figures 3* and *4* show the surface morphologies of titanium alloys IMI 834 and 6242, respectively, at 500, 600 and 700°C. The formed scale on IMI 834 was cracked and intact at 500°C and spalled at 600°C. While at 700°C, the scale was not only spalled but also the depth of the crack was significantly deep. In the case of 6242, the scale was intact at 500°C, cracked at 600°C and spalled at 700°C (*Figure 4*). However, the cracks are not as deep as that of IMI 834 at similar environmental conditions. The EDS results of hot-corroded IMI 834 and 6242 at various temperatures are shown in *Figures 5* and *6*. The EDS data of IMI 834 at all the temperatures show the formation of oxides of titanium, aluminium, tin and silicon. The peaks corresponding to sodium and chlorine are due to the presence of residual salt on the samples. In the case of 6242, the EDS data show the formation of oxides of titanium, aluminium, molybdenum and small amount of silicon at 500°C. When the temperature increased to 600°C, a very small amount of molybdenum in association with titanium and aluminium oxides was formed. While at 700°C, only the oxides of titanium and aluminium were observed and there was no presence of molybdenum or silicon. The formation of oxide scale clusters on the surface of titanium alloys at 500, 600 and 700°C, which gradually increased with increase in temperature, is responsible in degrading the alloys by affecting the mechanical properties that make them...
Figure 3. Surface morphologies of hot-corroded IMI 834 alloy at various temperatures.

Figure 4. Surface morphologies of hot-corroded Ti 6242 alloy at different temperatures.
unsuitable for marine gas turbine engine applications. However, the 6242 showed better performance when compared with IMI 834.

**Figure 5.** Electron dispersive spectroscopy (EDS) patterns of hot-corroded IMI 834 at different temperatures.

**Figure 6.** Electron dispersive spectroscopy results of hot-corroded 6242 at different temperatures.
2.4. Micro-hardness measurements

Micro-hardness profiles as a function of depth from the surface for hot-corroded IMI 834 and 6242 are presented in Figures 7 and 8, respectively. It is observed that the hardness is higher at the surface of the alloys than in the substrate. This is attributed to the corrosion that takes place at the surface. The high hardness is due to the dissolution of oxygen in the titanium alloys because of exposure to high temperatures in marine environmental conditions. The oxygen-dissolved region is also known as alpha case. It is also observed that the hardness gradually decreases from the surface to the substrate and finally becomes constant. The depth at which the hardness becomes a constant provides the depth of the alpha case. It is seen from the micro-hardness data that the depth of alpha case is more for higher temperatures due to increased corrosion rates at elevated temperatures. It is known that the corrosion rate increases with increase in temperature (Table 2). It is also evident from Figures 7 and 8 that the depth of alpha case is higher for IMI 834 compared to 6242 at all the studied temperatures.

Figure 7. Micro-hardness as a function of depth of α case for hot-corroded IMI834 at varied temperatures.

Figure 8. Micro-hardness as a function of depth of α case for hot-corroded 6242 at different temperatures.
2.5. Cross sections

The cross sections of hot-corroded titanium alloys IMI 834 and 6242 exposed at 500, 600 and 700°C are shown in Figures 9 and 10, respectively. The figures reveal that the corrosion-affected region increases with increase in temperature for both the alloys. However, the titanium alloy IMI 834 has more oxide scale at all the studied temperatures compared to Ti 6242. It is also clearly observed that the corrosion-affected zone is more for the hot-corroded IMI 834 when compared to Ti 6242 at all the temperatures. It indicates that Ti 6242 alloy provides good corrosion resistance and is suitable for marine applications.

Figure 9. Cross sections of IMI 834 after exposure to hot corrosion environment at various temperatures.
3. Comparative evaluation

Any material that is to be chosen for marine gas turbine engine applications should perform its function at service environmental conditions for a designed period. Therefore, suitable selection of a material is mandatory. It can be done based on extensive laboratory experimentation only because it is not possible to test the materials directly in the field. Therefore, comparative evaluation of titanium alloys IMI 834 and 6242 has been carried out under simulated marine gas turbine engine conditions. In order to compare the results precisely for both the alloys, the data were redrawn at different temperatures. The variation of weight change as a function of time for IMI 834 and Ti 6242 at temperatures of 500, 600 and 700°C is
Figure 11. Comparative weight change as a function of exposure time for Ti 6242 and IMI 834 at different temperatures.

Figure 11. Comparative weight change as a function of exposure time for Ti 6242 and IMI 834 at different temperatures.
compared as shown in Figure 11. There is a large difference in weight change as the time progresses till 100 h. For example, after 20 h the weight change for IMI 834 is 1.7 mg/cm² and it is 1 mg/cm² for 6242. As the time increased to 40 h, the weight change is increased to 2.5 mg/cm² for IMI 834 and 1.25 mg/cm² for 6242. With further increase in exposure time, the weight change increased marginally for both the alloys. After 60 h, the weight change remains constant for both the alloys. In essence, the weight change is almost doubled for IMI 834 compared to 6242 at 500°C indicating that IMI 834 is highly vulnerable to hot corrosion and corrodes at a faster rate. Similar behaviour is clearly observed at 600 as well as at 700°C (Figure 11) although the difference is less at 700°C. It is to be noted that the weight change is considerably more at 700°C for both the alloys. However, it is less for 6242 compared to IMI 834. This observation clearly shows that Ti 6242 is more preferable than IMI 834 for marine applications.

SEM results of IM 834 and 6242 show that the oxide scale cracked in the presence of marine environment. This indicates that the chloride ions present in the environment promote oxide scale cracking and facilitate oxygen diffusion into the alloy, which is the reason for observing significant weight change. Cross sections of hot-corroded specimens revealed the presence of an oxide scale and alpha case (Figures 9 and 10). The oxide scale consists of granular rutile and alumina. The region just below the oxide scale is the oxygen-dissolution region (α case). As expected, the thickness of the oxide scale increases with increase in temperature.

In order to understand the effect of hot corrosion of IMI 834 and 6242 more clearly, the microhardness data were redrawn at various temperatures. The depth of alpha case at 500°C is about 175 µm for 6242 and 300 µm for IMI 834. At 600°C, the depth of alpha case is about 200 µm for 6242 and 400 µm for IMI 834. While at 700°C, it is 500 µm for 6242 and 700 µm for IMI 834 (Figure 12). The results clearly indicate that the depth of alpha case is considerably high for IMI 834 than 6242 at all the temperatures. It indicates that the corrosion rate is much faster for IMI 834 compared to 6242. It is further evidenced by observing low corrosion-affected zone from the cross sections of both the alloys. The hardened zone due to diffusion of oxygen into the alloys exhibits a considerable surface hardness, which is sufficient to affect the mechanical properties of the titanium alloys by forming a highly brittle zone in which cracks initiate during service. The total depth of α-case formed for IMI 834 in marine environment is several times more than that of specimens oxidized in air at the same temperature. This clearly demonstrates the aggressiveness of marine environment compared to oxidizing conditions. Analysis of scales by XRD revealed the presence of TiCl₂, TiO₂, ZrCl₂, AlCl₃ and Al₂O₃ indicating that oxygen and chlorine present in the marine environment react with the alloy constituents to form their corresponding chlorides and oxides.

The present results suggest that the titanium alloy 6242 can be used for the fabrication of components intended for marine gas turbine engines. The investigations further suggest that effective protective measures are essential as the life of alloy improves significantly with appropriate protective coatings. Therefore, it is recommended to use titanium alloy 6242 instead of IMI 834 with appropriate protective coatings for marine gas turbine engine applications for their enhanced efficiency.
Figure 12. Comparative depth of alpha case for IMI 834 and 6242 at different temperatures.
4. Degradation mechanism

In general, titanium alloys containing less than 50 at.% aluminium do not form a continuous, dense and protective alumina scale upon exposure to elevated temperatures due to thermodynamic considerations [24]. IMI 834 and 6242 alloys containing only about 6 wt.% aluminium were not able to form a continuous, protective alumina scale. The oxide scale formed on the surface of IMI 834 and 6242 started spalling after exposure in marine environment indicating the formation of a poorly adherent oxide scale after reacting with chloride ions present in the environment. The previous results revealed that rutile formation is predominant followed by alumina on rutile at elevated temperatures [2, 3]. The XRD results show the formation of titanium and aluminium chlorides due to the fact that the titania readily reacts with chloride ions present in the environment to form chlorides at elevated temperatures. Given below are the proposed mechanistic steps that degrade IMI 834 and 6242 under marine environmental conditions:

1. The oxide scale that forms on the surface of IMI 834 and 6242 are predominantly TiO$_2$ in association with Al$_2$O$_3$. The TiO$_2$ reacts with chloride ions present in the marine environment to form volatile TiCl$_2$

   \[
   \text{TiO}_2 + 2\text{Cl}^- \rightarrow \text{TiCl}_2 + 2\text{O}^{2-} \tag{1}
   \]

   The TiCl$_2$ dissociates at elevated temperatures to form Ti$^{2+}$ and Cl$^-$ ions

   \[
   \text{TiCl}_2 = \text{Ti}^{2+} + 2\text{Cl}^- \tag{2}
   \]

   The titanium ions then react with oxygen ions present in the environment to form a non-adherent and non-protective TiO$_2$ scale, which spalls very easily. Chloride ions present in the marine environment penetrate into the alloy to form volatile chlorides. This process continues until titanium in the alloys is consumed. In other words, the reaction is autocatalytic. The oxygen ions that form in the above reaction diffuse into the alloy and form an oxygen-dissolution region due to more solubility of oxygen in titanium alloys.

2. Al$_2$O$_3$ reacts with Cl$^-$ ions to form aluminium chloride

   \[
   \text{Al}_2\text{O}_3 + 6\text{Cl}^- \rightarrow 2\text{AlCl}_3 + 3\text{O}^{2-} \tag{3}
   \]

   The AlCl$_3$ that formed in the above reaction dissociates to form Al$^{3+}$ and Cl$^-$ ions

   \[
   \text{AlCl}_3 = \text{Al}^{3+} + 3\text{Cl}^- \tag{4}
   \]

   The Al$^{3+}$ ions react with oxygen ions to form a loose and non-protective alumina scale, which spalls very easily, as in the case of titania.
Here again, the chloride ions penetrate into the titanium alloy to form volatile chlorides. As mentioned above, the reaction is autocatalytic. The oxygen ions that formed in reaction (3) diffuse into the alloy and react with the alloys. Both the above processes (reactions (1) and (3)) contribute to the formation of α case in the titanium alloys subsurface.

As a result of the above reactions, the degradation of titanium alloys takes place at a faster rate. The results of Du et al. [25] provide evidence for the proposed mechanism. This mechanism is also supported by the significant depth of α-case formation (Figure 12) as well as weight change (Figure 11) in the marine environment. Further, SEM results clearly show cracking of the oxide scale in marine environments (Figures 3 and 4). Once the cracks are formed in the oxide scale, because of the formation of volatile chlorides, oxygen can penetrate more easily into the alloy and form the oxygen-dissolution region at a faster rate. This is the reason for the significant depth of α case in marine environments. The proposed mechanism is supported by the reported literature [26, 27]. This cracking situation easily makes the components fabricated from IMI 834, susceptible to failure under normal service conditions of the compressor section of gas turbines. This mechanism is evidenced by observing stress-corrosion cracking in titanium alloys in the presence of halides and stress [26, 27]. It was also reported that the extent of attack depends on temperature, exposure time and tensile stress [28, 29]. Cracking in titanium alloys was also reported by Bauer [30] who traced the crack origins. It is further supported by Beck, who reported cracking in stressed Ti-8Al-1Mo-1V alloy when immersed in anhydrous LiCl-KCl eutectic at 707 °F [31]. Even in actual jet engines, cracking was observed on salted Ti-6Al-4V alloy discs, indicating comprehensive evidence for the suggested mechanism [32]. It is well agreed by researchers in the field that NaCl is the more severe environment [33]. It was also mentioned that a liquid phase is not essential for causing cracking. Chemical periodicity is also not a factor. What appears pertinent is the reactivity of the salt in penetrating titanium oxide and in developing brittle products. The cracking mechanism is well supported by Logan et al. [34]. They proposed that oxygen ions from the scale and chlorine ions from the NaCl diffuse into the titanium alloy, react with alloy constituents to destroy atomic-binding forces and cause cracking. In essence, the reported literature clearly provides sufficient evidence for the proposed mechanism. It suggests the necessity of protecting titanium alloy components from hot corrosion to eliminate failures during service and thereby enhance their life. The studies also stress the need to develop coatings to protect titanium alloys from both oxidation and hot corrosion that are experienced by gas turbine engine compressor section components.

5. Smart coatings development

Various smart coatings containing iridium, tungsten, palladium, tantalum, aluminium and their combination were designed and developed on titanium alloy, IMI 834, using various
surface engineering techniques and investigated systematically under both oxidation and hot corrosion conditions [35]. The results revealed that the smart coatings based on aluminium that were developed by innovating a new-pack composition showed an excellent resistance under both oxidation and hot corrosion conditions [35, 36]. The elemental distribution showed a protective, continuous and adherent alumina scale over the coating during both oxidation and hot corrosion conditions [36]. The XRD patterns of oxidized and hot-corroded smart coatings revealed that the major phase in the scale was primarily alumina [36]. No outward diffusion of alloying elements such as Sn, Zr, Mo and Nb was noticed. In addition, there was no inward diffusion of oxygen or nitrogen observed. Further, micro-hardness measurements made on oxidized and hot-corroded smart coatings indicated that there was no hardened zone formed, whereas the oxidized and hot-corroded uncoated alloys showed a significant hardened zone [36]. It indicates that an excellent protection was provided by the designed and developed smart coating based on aluminium to the titanium alloys from oxidation, alpha-case formation as well as hot corrosion. Modern gas turbines need to operate at high temperatures for their enhanced efficiency and the high-temperature oxidation; α-case formation and hot corrosion are the major concerns as mentioned above. The developed coating exhibited an excellent oxidation and hot corrosion resistance to the titanium alloys, prevented alpha-case formation effectively, and thus the smart coated titanium alloy components can be used safely at higher temperatures for achieving enhanced efficiency. Further, the developed coatings can be prepared by a simple technique, easy to coat large components and moreover highly economical. Hence, it is recommended to use the designed and developed smart coatings for the modern gas turbine engine titanium alloy components.

6. Summary

Hot corrosion problems in marine gas turbine engine compressor section components fabricated from titanium-based alloys along with their degradation mechanisms have been explained in detail by systematically studying the titanium alloys 6242 and IMI 834 in simulated marine gas turbine engine conditions. The ingress of oxygen increases with time and temperature, which causes to form hardened zone that initiates crack formation and ultimately fails the components. The importance of selecting suitable titanium alloy, which exhibits good hot corrosion resistance for fabrication of compressor components, has been stressed. The development of smart coatings based on newer composition of elements and their combination has been explained and showed that among the developed coatings, a smart coating based on aluminium that was deposited by innovating new-pack composition exhibits an excellent protection to the titanium alloys against oxidation, alpha-case formation and hot corrosion, which in turn enhances the efficiency of modern gas turbine engines of various types, that is, aero, marine and industrial. Therefore, it is recommended to use the titanium alloy 6242 in association with developed smart coating for advanced marine gas turbine engine compressor section components for their enhanced service life and maximum efficiency.
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