Evaluation of Solution Treated Ti-15-3 Alloy for Naval Fastener Applications

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Abstract

Environmentally induced degradation is a serious issue governing the use of titanium alloy fasteners for marine applications. The work horse alloy Ti6Al4Vwhich has beenthe most used titanium alloy till date as fastener material has its limitations and search has been on for improved titanium based materials. This paper deals with researches aimed at evaluating the metastable beta titanium alloy Ti15V3Cr3Al3Sn (Ti15-3)in solution annealed condition as a fastener material for medium strength applications. A variety of tests was carried out to rate the resistance of the alloy in this condition to seawater environments– slow strain rate testing (SSRT), crevice corrosion testing, potentiodynamic polarization studies and immersion testing. Limited SSRT was also done on Ti6Al4V for the sake of comparison. Analysis of test results shows that

solution annealed Ti15-3 offers itself as a good candidate material for medium strength fastener applications in marine environments.

Keywords: Titanium alloy, Fastener application, Marine environment, Environmental degradation, Slowstrain rate testing, Potentiodynamicpolarization, Crevice corrosion

Introduction

Titanium has been used as a fastener material over last five to six decades. The Titanium grade which found largest usage in aerospace and automotive sectors is Ti6Al4V. However the limited cold-formability and the poor hardenability have been disadvantages which necessitated development / evaluation of other titanium base alloysfor fastener applications. The poor cold formability added to the cost of manufacture and the poor hardenability came as a limitation to produce high strength fasteners in large sizes (>~19 mm in diameter)(Ref 1-3).Beta-rich $\alpha+\beta$ titanium alloys and metastable beta titanium alloys have received much attention in this context.They have a better cold formability as also better hardenability than Ti6Al4V alloy(Ref 4, 5).Ferrero (Ref 6)examinednine titanium alloys belonging to these two groups as candidate materials for high strength fastener applications in both the aerospace and automotive industries and came to the conclusion that prima-facie all of them are suitable.

Even in marine environments titanium alloys have had an important place as fastener materials, as they are virtually immune to seawater corrosion. Being the most widely produced and used alloy, Ti6Al4V received the first attention even for marine applications. However there has been a concern about its reduced levels of fracture toughness in seawater, leading to evolution of extra low interstitial variant of Ti6Al4V

(Ti6Al4V ELI) for critical seawater applications. Ti6Al4V ELI is known to have higher fracture toughness over the standard grade Ti6Al4V in both air and seawater environments. Attention was at the same time devoted to development of other titanium based alloys for naval fastener applications. The near-alpha alloy Ti5Al1Sn1Zr1V0.8Mo (Ti-5111) was shown to have several attractive attributes for medium strength marine fastener applications(Ref 7). With reference to passing the wedge tensile test, stress corrosion cracking in marine environments and cold formability, superiority of Ti-5111 over Ti6Al4V was brought out (Ref 7). Attention was also devoted to metastable β and β-rich α+β titanium alloys, particularly for high strength fastener applications, in view of their good workability, excellent hardenability and heat treatability to high strength levels. Esaklul and Ahmed (Ref 8)made detailed study of failures of high strength fasteners in use in offshore and subsea applications andshortlisted three metastable beta titanium alloys - Ti10V2Fe3Al, Ti15V3Al3Cr3Sn and Ti15Mo2.7Nb3Al0.2Si - as having good potential for application as fasteners for subsea applications, based on the high strengths to which they can be produced, high hardenability and good resistance they are expected to possess to environmentally assisted cracking.

The present research deals with evaluation of Ti15-3 in solution annealed condition as a medium strength fastener material for naval applications. The alloy can be heat treated to high strength levels by aging (Ref 9). In the aged condition it is an attractive candidate material for high strength fastener applications, as reported in detail by SumanSakya et al(Ref 10). However, aging leads to a significant reduction in the resistance offered by the material to degradation in naval environments (Ref 10). Further thread rolling of beta titanium alloysin aged condition for manufacture of fasteners has given rise to many problems (Ref 6). Thecritical strength criterion for designing tensile loaded fastener assemblies is yield strength. Ultimate tensile strength is far less important.Ti15-3in solution annealed condition possesses yield strength and percent elongation comparable to Ti6Al4V ELI variant and Ti-5111 as shown in Table 1.Results for Ti15-3 in solution annealed condition have been drawn from Matweb-Material Property Data (Ref 11) and work done at the laboratory of the corresponding author (Ref 12).Corresponding property data for Ti6Al4V is also included in the Table for ready comparison. Solution annealedTi15-3, like the other titanium grades shown in Table 1, hashigh yield strength to UTS ratio, bringing in considerable strength and safety advantage in applications using steel fasteners with similar UTS values(Ref 7). The fasteners may also experience some level of cyclic loading, failure generally occurring in the threaded section where stress concentrations are the highest or under the head. Ismarrubie et al (Ref 13) determined the fatigue life of Ti15-3 alloy in (i) solution treated and (ii) solution treated and aged condition.The fatigue life at 10^8 cycles to UTS ratio was found to be higher in the former condition. The relatively low fatigue limit of Ti15-3 in solution treated and aged condition arises from the tendency for inhomogeneous precipitation of α phase in β matrix on aging (Ref 12).

Different types of evaluation have been carried out on solution annealed Ti15-3 as part of the present research to evaluate it as a medium strength fastener material for seawater environments. These includeslow strain rate testing (SSRT), crevice corrosion testing,potentiodynamic polarization studiesand weight loss by immersion testing. SSRT was demonstrated to be very effective technique for ranking the materials based on their susceptibility to environment-induced degradation (Ref 14). Fastener installations naturally create crevice geometries that in susceptible materials lead to crevice attack. Crevice corrosion testing thus becomes highly critical for evaluation as fastener material. SSRT was carried out on a comparative basis on Ti6Al4V, the most used titanium alloy for fastener applications.

Material and Experimental methods

The Ti15-3 beta titanium alloy used in this investigation was supplied by M/s GE Wick (China). The material was in solution treated condition. Solution treatment was carried out above the β transus temperature and accordingly the microstructure is one of single phase β. The material was in the form of sheet, 3 mm in thickness. SSRT was also carried out on Ti6Al4Vα+β titanium alloy, also supplied by M/s GE Wick. The material was in the mill annealed condition. Details of chemical composition are given inTable 2. The mechanical properties are shown in Table 3.

SSRT was carried out on Ti15-3 material in solution annealed condition. Three strain rates were used for testing – 10^{-5}, 10^{-6} and 10^{-7} s^{-1}.Testing was done in three different environments (i) air having relative humidity of ~ 35 % (referred to as 35 % RH air) (ii) synthetic sea water and (iii) 3.5 % NaCl solution in water (referred to as 3.5 % NaCl). The synthetic sea water was prepared by the method devised by Kester (Ref 15).Tests were allcarried outat ambient temperature. Comparative SSRT was carried out on Ti6Al4V material in mill annealed condition. However, testing was done at only one strain rate (10^{-6} s^{-1}) and only in two environments (35 % RH air and 3.5 % NaCl). The details of single edge notched flat specimen used for SSRT are given elsewhere (Ref 10).

The susceptibility to cracking in synthetic sea water/ 3.5 % NaCl was calculated as:

(i) As the ratio of time to failure:

$$\text{Ratio of time to failure} = \frac{\text{Time to failure in corrosive environment}}{\text{Time to failure in 35 \% RH air}} \qquad (1)$$

(ii) As percent loss of plasticity:

$$\text{\% loss of plasticity} = \frac{\text{\% Elongation in 35 \% RH air} - \text{\% Elongation in corrosion environment}}{\text{\% Elongation in 35 \% RH air}} \qquad (2)$$

(iii) As fractional loss of notched tensile strength (NTS):

$$\text{\% loss of notched tensile strength} = \frac{\text{NTS (in 35 \% RH air)} - \text{NTS (in corrosive environment)}}{\text{NTS (in 35 \% RH air)}} \qquad (3)$$

Crevice corrosion testing was done on Ti15-3 material in solution annealed condition in accordance with ASTM G48 standard (Ref 16). The specimen preparation was carried out conforming to the requirements of ASTM G1 standard (Ref 17). The as-received sheets were cut into test specimens 25 mm x 50 mm in size. A hole of 1 cm diameter was drilled in the center of the specimen by electro discharge machining. A titanium bolt was placed in the hole and Teflon washers having number of grooves and plateaus were fitted. A titanium nut was threaded on to the bolt and a torque of 0.28 N .m was applied using a drive torque limiting nut driver. Figure 1 shows the sample fitted with bolt and washers. Corrosion testing was carried out in three different media - (i) 6 %

$FeCl_3$+ 1 % HCl (acidified ferric chloride) (ii) 10 % $FeCl_3$ and (iii) Green Death solution comprising of 11.9 % H_2SO_4 , 1 % $FeCl_3$, 1 % $CuCl_2$, 1.3 % HCl and the rest water. Tests were carried out for 72 h in case of 6 % and 10 % $FeCl_3$ solutions and 24 h for the Green Death solution. The number and depths of attacked sites were recorded. Tests were carried out at constant temperature, test temperature varying in the range 65-90 ^{o}C. Weight loss was also monitored in all cases.

Potentiodynamic polarization testing on Ti15-3 material was carried out in 3.5 % NaCl at 25 ± 1 ^{o}C according to ASTM G5 standard (Ref 18), using the Electrochemical Work Station Model IM 6 e, ZAHNER GmbH, Germany. Measurements were conducted in the range –700 to 250 mV with reference to open circuit potential at a scan rate of 2 mV/s to determine the corrosion parameters – corrosion current (I_{corr}) and corrosion potential (E_{corr}). A three electrode cell assembly with Ti15-3 as working electrode with an exposed area of 1 cm^2, an Ag/AgCl/1M KCl electrode as reference electrode and platinum electrode as counter electrode was used. The specimen was prepared conforming to the requirements of ASTM G1.

Immersion corrosion testing in 3.5 % NaCl at 25 ± 1^{o}C was performed on Ti15-3 samples in solution annealed condition; weight loss resulting after immersion for 30 days was determined.

Results and Discussion

Slow Strain Rate Testing

Notched tensile specimens were subjected to SSRT at three different strain rates (10^{-5}, 10^{-6} and 10^{-7} s^{-1}) in three different environments – 35 % RH air, synthetic seawater and

3.5 % NaCl under freely corroding conditions. The environment-to-air ratios of time to failure are in the range 0.92-0.96 for synthetic seawater and 0.94-0.99 for 3.5 % NaCl. The values are all very close to 1.0 indicating excellent resistance to corrosion. The % loss of notched tensile strength values are in the range 0.4-3.1 for synthetic seawater and 0.2-2.0 for 3.5 % NaCl. The values are all very small again suggesting an excellent degree of corrosion resistance. The % loss of plasticity values are in the range 7.0 – 15.0 for synthetic seawater and 5.1 – 6.9 for 3.5 % NaCl. These numbers again suggest that the plasticity is largely retained in both corrosive environments. Table 4 shows the details.

Comparative SSRT was carried out on alloy Ti6Al4V, but at only one strain rate ($10^{-6}s^{-1}$) and only one corrosive environment (3.5 % NaCl). Table 5 compares the ratio of time to failure, % loss of plasticity and % loss of notched tensile strength for Ti15-3 and Ti6Al4V. Ti15-3 shows distinctly lower susceptibility to damage in 3.5 % NaCl compared to Ti6Al4V. The Ti15-3 has somewhat lower strength but higher ductility compared to Ti6Al4V in the tested condition (Table 3).

Crevice Corrosion Testing

Testing at 65 ^oC and 70 ^oC in 6 % $FeCl_3$ + 1 % HCl solution resulted in no crevice formation. At 90 ^oC there was initiation of corrosion damage and weight loss of 0.003 g was observed. Testing at 70 ^oCin 10 % $FeCl_3$ resulted in no crevice formation; testing at 90 ^oC resulted in corrosion attack with an associated weight loss of 0.004 g. Testing at 70 ^oC in Green Death solution resulted in no corrosion attack. However, testing at 85 ^oC in this medium led to attack and a weight loss of 0.101 g. Testing at 90 ^oC led to higher degree of attack and a higher weight loss (0.165 g). Table 6 shows the results obtained.

Testing in acidified 6 % $FeCl_3$solution for evaluating the critical crevice temperature is covered by ASTM G-48 for ranking, with respect to crevice corrosion resistance, stainless steels, nickel base alloys and chromium-bearing alloys. However use of testing in $FeCl_3$ solutions has been done for evaluating the relative crevice corrosion resistance of different titanium grades and for comparing the crevice corrosion resistance of titanium grades with that of superalloy grade 625 (Ref 19). That there was no corrosion attack at temperatures$\leq$ 70 ^{o}C for all the three corrosive environmentspoints to a high resistance to crevice corrosion of alloy Ti15-3. 10 % $FeCl_3$solution was found to be more corrosive than 6 % $FeCl_3$ + 1 % HCl solution. Expectedly Green Death solution was found to bethe most corrosive of all the solutions.

Potentiodynamic Polarization Studies

The potentiodynamic polarization curve of Ti15-3in 3.5 % NaCl at 25 ± 1^{o}C is shown in Fig. (2).In terms of molarity, the concentration works out to 0.6 M. The corrosion current (I_{corr}) and corrosion potential (E_{corr}) were determined from the polarization curve using the Tafel extrapolation method; the values are shown in Table 7.

Shahba et al. (Ref 20)carried out similar studies on Ti6Al4V alloy in NaCl solutions of various concentrations and results for 0.5 M and 1.0 M NaCl solutions from their studies are included in Table 7for comparison.According to these authors, Ti6Al4V material becomes much more susceptible to corrosion as the concentration of the NaCl solution increases from 0.5 to 1.0 M, with E_{corr}becoming more negative and I_{corr}increasing very steeply. It is seen that Ti6Al4V shows substantially more negative E_{corr}values, indicating that it is more susceptible to corrosion in 3.5 % NaCl than Ti15-3. Further, the I_{corr}values of Ti6Al4V are higher indicating its higher susceptibility to corrosion in 3.5 % NaCl. A one to one comparison is not warranted, considering that the two sets of measurements were done at two different laboratories and at different points of time. However, for the purpose of ranking the two alloys with respect to susceptibility to corrosion in seawater environment, the comparison is considered reasonable.

Immersion Testing

The corrosion rate in 3.5 % NaCl(0.6 M NaCl) based on results obtained onTi15-3 samples immersed in solution for 720 hours works out to 0.3135 mpy. The corrosion rate calculated by Shahba et al (Ref 20) for Ti6Al4Vin 0.5 MNaClsolution is 25.68 μm/yr (1.01 mpy). They also reported increasing corrosion rate with increasing molarity. Corrosion rate calculated forTi15-3 in the present study is thus substantially lower. Weight loss obtained in the present study is based on immersion testing, while Shahba et al (Ref 20) arrived at the weight loss through electrochemical measurements.For this reason a one to one comparison is not possible. However it is believed that a ranking of the materials is still in order.

Beta alloys are inevitably designed for use in the age hardened condition, as high strength levels can be obtained after aging. Further, the advantage of these alloys lies in that large sized fasteners can be produced with high strength, thanks to their high hardenability. All the published literature making reference to the potential applications of beta titanium alloys for high strength fastener applications alludes to the age hardened condition of these alloys. The present research is a deviation from this approach and deals instead with potential use of the metastable beta titanium alloy Ti15-3in solution treated condition for medium strength fastener applications in naval environments. The advantage of working with the solution treated condition lies in the higher resistance the material offers to corrosion in seawater environments compared to the aged condition. Further, The Ti15-3 has a much higher cold formability in the solution treated condition compared to Ti6Al4V; this is expected to substantially bring down the manufacturing cost. The metallurgical stability of thesolution treated alloy at temperatures ≤200 ^{o}C has been well demonstrated (Ref 12); as such there may be no apprehension about using fasteners in this condition, so long as service temperatures are below 200 ^{o}C.Considering the advantages offered by solution treatedTi15-3 such as high resistance to environmental degradation, excellent cold formability, the alloy can also be considered for fastener applications in this temperature range in aerospace sector.

Conclusions

1. Slow strain rate testing indicates that alloy Ti15-3 in solution annealed condition shows excellent resistance to corrosion in 3.5 % NaCl and synthetic seawater environments. Ti15-3 in solution annealed condition shows higher resistance to degradation than Ti6Al4V in mill annealed condition.

2. The alloy Ti15-3 in solution annealed condition shows excellent resistance to crevice corrosion, with critical pitting temperature in acidified $FeCl_3$solution > 70 ^{o}C. The resistance to crevice corrosion decreases in the following order: acidified 6 % $FeCl_3$→10 % $FeCl_3$→Green Death solution.

3. Comparing the results ofpotentiodynamic polarization study carried out in the present research on solution treated Ti15-3 in 3.5 % NaCl with those obtained from similar studies carried out by earlier researchers on Ti6Al4V,it is seen that Ti15-3 shows less negative value of corrosion voltage (E_{corr}) and lower value of corrosion current than Ti6Al4V. This would mean substantially lower corrosion rates of Ti15-3 in 3.5 % NaCl compared to Ti6Al4V.

4. Immersion corrosion testing of Ti15-3 in 3.5 % NaCl shows minimal weight loss, pointing to high corrosion resistance of the alloy.

5. Based on the conclusions 1 to 4, it clearly emerges that Ti15-3 is more resistant to degradation in seawater environments. Taking into account the good cold formability of Ti15-3, it is believed that Ti15-3 would be a better alternative to Ti6Al4V for medium strength fastener applications in marine environments.

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Table and Figure Captions

Table 1

Comparison of mechanical properties of titanium alloys for fasteners applications

Material	0.2 % Ys (MPa)	UTS (MPa)	% Elongation	Remarks
Ti6Al4V	862	1034	10	Data obtained from Ref

Ti6Al4V ELI	887	965	15	Data obtained from Ref
Ti 15-3 Solution annealed	780	820	16	For strip / sheet ; Data obtained from mat web- Material property data (11)
Ti 15-3 Solution annealed	775	805	13	Unpublished results
Ti-5 111	753	862	15	Average values obtained on round rod materials

Alloy	Ti	V	Cr	Sn	Al	Fe	C	N	H	O
Ti15-3	remaining	15.1	3.0	3.1	3.0	0.18	0.008	0.027	0.003	0.009
Ti6-4	remaining	4.0	-	-	6.0	0.1	0.03	0.01	0.003	0.15

Table 2 Chemical Composition of Ti15-3 and Ti6-4 (in weight %)

Table 3 Strength and ductility values of the alloys in the tested condition

Material	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	% Elongation

Ti 15-3 in solution treated condition	770	790	22
Ti6-4 in mill annealed condition	880	950	14

Table 4 Ratio of time to failure, percent loss of ductility and percent loss of notched tensile strength for Ti15-3 alloy for the three strain rates tested

	Synthetic Sea Water			3.5 % NaCl		
Strain rate (S^{-1})	Ratio of time to failure	Percent loss of plasticity	Percent loss of notched tensile strength	Ratio of time to failure	Percent loss of plasticity	Percent loss of notched tensile strength
10^{-5}	0.96	7.0	0.4	0.99	5.1	0.2
10^{-6}	0.95	7.5	3.1	0.98	6.2	2.0
10^{-7}	0.92	15.0	2.8	0.94	6.9	1.9

Table 5 Comparative performance of Ti 15-3 and Ti 6-4 in 3.5 % NaCl environment strain rate 10^{-6} S^{-1}

	Ti 15-3	Ti 6-4
Ratio of time to failure	0.99	0.92
Percent loss of plasticity	6.2	11.2
Percent loss of notched tensile strength	2.0	2.5

Table 6 Results of Crevice Corrosion Testing

Solution used	Temperature (^{o}C)	Weight loss (g)	No. of sites attacked	Max. depth of crevice observed (mm)	Average crevice depth	Crevice index
6 % $FeCl_3$ by mass and 1 % HCl	65	Nil	0	-	-	0
6 % $FeCl_3$ by mass and 1 % HCl	70	Nil	0	-	-	0
6 % $FeCl_3$ by mass and 1 % HCl	90	0.003	5	0.02	0.012	0.1
10 % $FeCl_3$ by mass	70	Nil	0	-	-	0
10 % $FeCl_3$ by mass	90	0.0043	5	0.023	0.015	0.161
Green death	70	Nil	0	-	-	0

Solution						
Green death Solution	85	0.1010	8	0.034	0.021	0.272
Green death Solution	90	0.1649 (fastener got visible corroded)	9	0.07	0.034	0.63

Table 7

Electrochemical corrosion parameters obtained from potentiodynamic polarization curves in 3.5 % NaCl solution at 25 ± 1^{o}C

Alloy	E_{corr} (μV)	I_{corr}(μA / cm^{2})	Comments
Ti 15-3	-145.4	0.539	3.5 % NaCl solution (0.6 M NaCl solution)
Ti 6Al4V	-769.7	2195	0.5 M NaCl solution (Shahba et al)
	-754.1	1.5	1 M NaCl solution (Shahba et al)

List of Figures

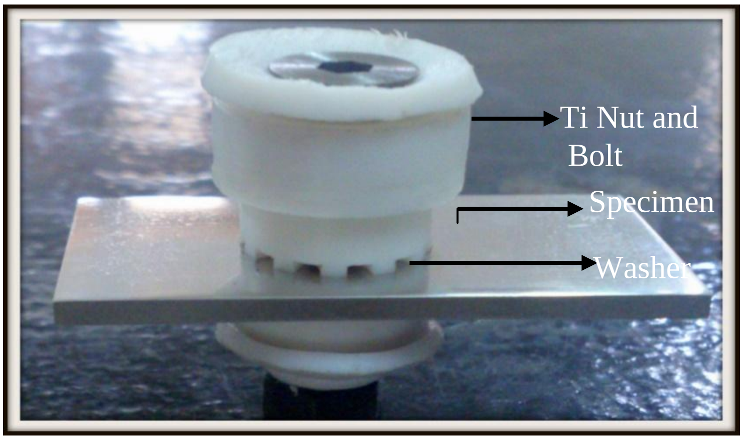

Figure 1 Sample fitted with bolt and washers

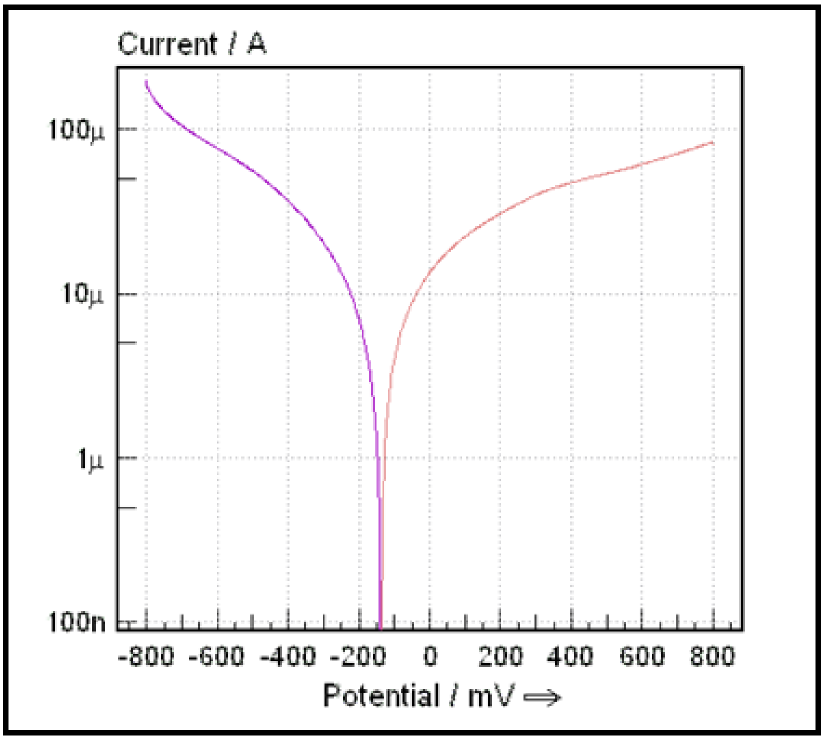

Figure 2 Potentiodynamic Polarization Curve for Ti 15-3 alloy in solution treated condition