CORROSION AND STRESS CORROSION CRACKING OF COMMERCIAL TITANIUM IN METHANOL—BROMINE SOLUTION

H. V. Sudhakar Nayak, K. I. Vasu and Y. V. R. K. Prasad

Department of Metallurgy, Indian Institute of Science, Bangalore-560012.

(Received and accepted Feb. 1978)

The failure of commercial titanium due to corrosion and stress corrosion in methanol-bromine solution is examined. The cracking in annealed titanium was found to be intergranular while the cold rolled titanium exhibited total immunity to corrosion and stress corrosion. The activation energy for the stress corrosion cracking of annealed titanium was estimated to be 38.5 KJ mole^{-1}. This value as well as the influences of other variables studied including stress, bromine concentration, water content, grain size, etc., are all in favour of a mechanism involving crack initiation due to anodic dissolution and halogen ion adsorption. The results also suggest that the crack initiation is an important step in deciding the SCC failure.

The failure of unalloyed titanium by severe intergranular corrosion was observed in methanol—halogen solutions by Tomashov, et al[1]. The stress corrosion cracking (SCC) of unalloyed titanium has also been observed in methanol solutions containing chlorine[2,3], bromine[4] or iodine[5], irrespective of whether the halogen was added as the element in molecular form[4,5], acid[2] or sodium salt[3]. Several models were suggested for SCC of unalloyed titanium in methanol—halogen solutions. Sedriks, et al.,[6,7] suggested the mechanism of stress—assisted localized anodic dissolution at the grain boundaries. It was also advocated[8] that there is interaction of halide ion with titanium which may take the form of adsorption or dissolution of the metal. Scully, et al.,[9] proposed the interaction of hydrogen with titanium, which may take the form of either entry of hydrogen into the lattice producing hydrogen embrittlement or the adsorption of hydrogen at the crack tip. The purpose of this paper is to study the corrosion characteristics and susceptibilty to SCC of commercial titanium in methanol—bromine solution and to evaluate the mechanisms of failure under susceptible conditions.

EXPERIMENTAL

The composition and mechanical properties of the material employed are given in Table 1. The starting material was 5 mm thick which was further cold rolled to 1 mm thickness. Sheet specimens for corrosion, stress corrosion and tensile tests were machined with their tensile axes in the rolling direction. The specimens had a gage length of 20 mm and a width of 4 mm. The machined specimens were annealed in a dynamic vacuum of 2.67×10^{-3} Nm^{-2} at 1100 K for 2 hours and subsequently furnace cooled. The resulting grain diameter as measured by linear intercept method was 51μm. Different grain sizes were produced by varying the temperature and time of annealing; the annealing treatments and the resulting grain diameters and other mechanical properties are listed in Table 2.

Experiments were also conducted on specimens which were cold rolled to about 80% reduction in thickness.

The environment used was methanol—0.8 $^{v}/_{o}$ bromine solution (pH = 0) which was prepared from reagent grade chemicals. The water content of this medium was estimated by Karl Fischer's method[10].

The time to failure of the specimens totally immersed in the corrosive medium was estimated by stressing them in a constant load machine. In this machine, the load is applied through a lever arm with 1:10 ratio and there is also a facility for recording the time to failure. The temperature of the test was controlled by a thermostat set-up. Some dynamic stressing experiments were also carried out on a constant strain rate tensile testing machine.

RESULTS

Annealed titanium when exposed to methanol—bromine solution exhibited extensive intergranular attack (Fig. 1) without appreciable weight loss. The



Fig. 1 Grain Boundary corrosion attack in alpha titanium exposed to Methanol — Bromine solution (80X)

corrosion was found to be very severe when the specimens were soaked in the solution for longer periods extending over a few days. In an extreme case, the specimens crumble to a powder as a result of the intergranular attack. The tensile properties of the annealed specimens before and after soaking are given in Table 3. For annealed specimens there was a loss in the strength along with a significant drop in the ductility. On the other hand, titanium specimens when cold rolled were found to be resistant to corrosion. There was no noticeable grain boundary attack or weight loss. Table 3 shows that the tensile strength and elongation were unaffected by soaking in the corrodant.

The potential variation with time as measured against SCE using an electrometer in annealed and cold rolled titanium are shown in Fig. 2. The potential—time curve for the annealed titanium shows a peak after 20 min. following immersion while this is reached almost instantaneously for the cold rolled specimen.

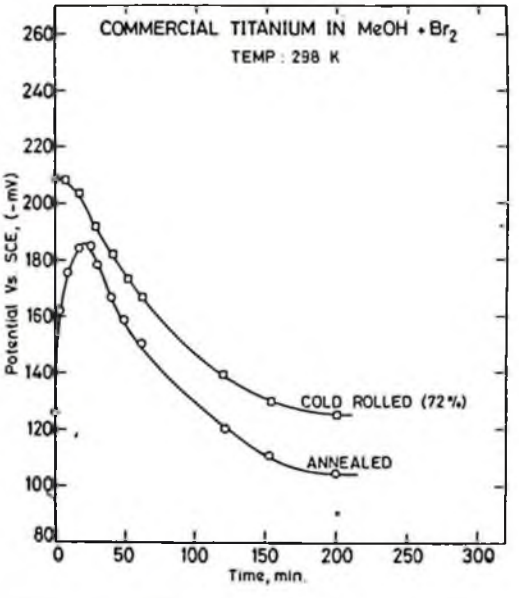


Fig. 2 POTENTIAL-TIME CURVES FOR ANNEALED AND COLD ROLLED (72% REDUCTION IN THICKNESS) COMMERCIAL TITANIUM.

The failure of the annealed titanium when subjected simultaneously to stress and corrosive medium ($MeOH + Br_2$) was examined. The material was found to be susceptible to SCC in this environment and the microstructure (Fig. 3) shows an intergranular type of attack. The loss in weight of the

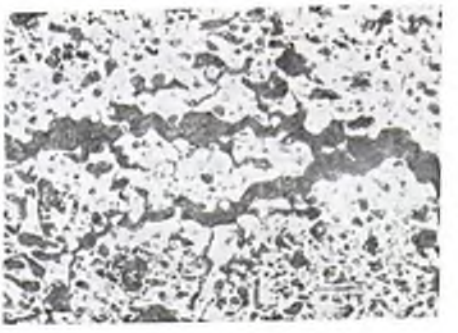


Fig. 3 Intergranular stress corrosion cracking in alpha titanium immersed in Methanol—Bromine solution (80X)

specimen subjected to different levels of stress and exposed to corrodant was measured and found to increase from 0.03% at 35% UTS to 0.1% at 52% UTS. In Fig. 4 is shown the effect of the stress level

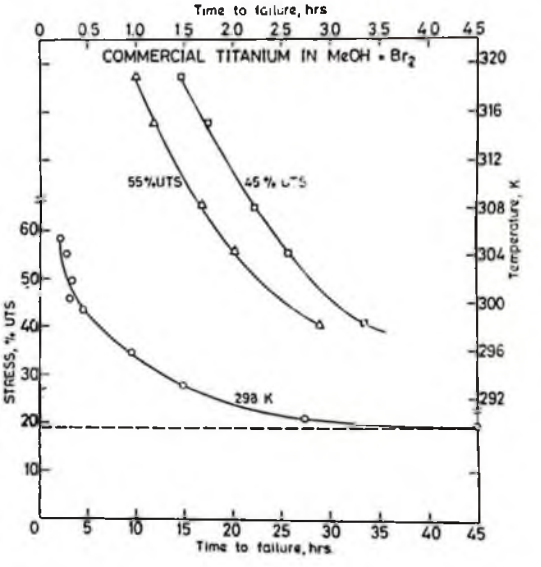


Fig. 4 DEPENDENCE OF TIME TO SCC FAILURE ON STRESS AND TEMPERATURE.

and temperature on the time taken for failure of the annealed titanium. There is a 'threshold' stress ($\sim$ 20% of UTS) below which the specimens will not fail by SCC. Increasing temperature of the medium enhances the susceptibility to SCC. The influences of the concentration of bromine in the $MeOH + Br_2$ solution, the water content, the period of ageing the solution and the period of soaking the specimen before the testing, on the time taken for failure are documented in Fig. 5. The bromine concentration upto about 1.5 % has considerable effect on stress corrosion

life—this effect being temperature dependent. The SCC was severe at a critical value of water content (0.1 %). The ageing of the solution and the pre-soaking of the specimen have detrimental effects on the SCC life of the annealed titanium specimens. The effect of grain size on the life of the specimen under SCC is given in Table 4. Coarse-grained specimens are highly susceptible to SCC.

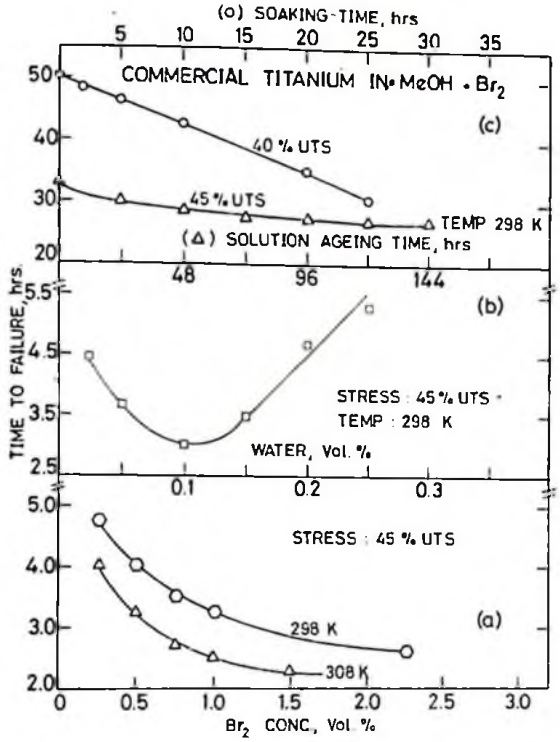


Fig. 5 DEPENDENCE OF TIME TO SCC FAILURE ON
(a) BROMINE CONCENTRATION
(b) WATER CONTENT AND
(c) SOLUTION AGEING AND SOAKING PERIODS

The cold rolled specimens were found to be totally immune to SCC. Even with stresses of the order of 80% of their UTS and under most aggressive conditions, the specimens did not show any tendency for cracking.

DISCUSSION

The nature of the corrosion damage in annealed titanium is essentially an intercrystalline (or localized) attack. Due to their anodic nature, the grain boundaries are preferentially dissolved in the corrosive medium giving rise to grain separation as an extreme consequence. This is the only process by which corrosion of titanium takes place because there is no loss in weight or uniform attack over the whole surface of the specimen. The potential-time curve for annealed titanium (Fig. 2) indicates two different stages: Initially an active region exists during which the metal dissolution occurs. This is followed by a region wherein the passivating film continuously being formed and ruptured. When the specimen is subjected simultaneously to stress, the passivating film breaks down due to plastic deformation and stress corrosion cracks are initiated. These cracks later propagate under tensile stresses and lead to failure. There are three major mechanisms that were suggested to explain the stress corrosion crack propagation in titanium and its alloys. These are based on: (1) intergranular anodic dissolution process assisted by stress[6,7], (2) interaction of halide ions with titanium at the crack tip causing adsorption of the halide ion resulting in the rupture of atomic bonds[8] and (3) hydrogen absorption leading to the formation of hydride nuclei on the operating slip planes resulting in cleavage cracking.

As the mode of cracking in annealed titanium is totally intercrystalline, it is not reasonable that the hydrogen embrittlement mechanism is responsible for the failure inasmuch as this mechanism suggests[9] transcrystalline or cleavage cracking. Further, it is observed that the time to failure under SCC conditions is a function of halide ion concentration (Fig. 5) which cannot be accounted for on the basis of the hydrogen embrittlement mechanism. On the other hand from the effect of temperature on the time to failure at a constant stress, which follows Arrhenius relation (Fig. 6), the activation energy is estimated to be 38.5 KJ $mole^{-1}$. This value matches with the activation energy estimated for the dissolution of titanium ($Ti \rightarrow Ti^{3+}$) in $MeOH + Br_2$ solution[11]. It is also reported[12] that the activation energy for the adsorption of halide ions at the crack tip may also be of the order of 15 to 35 KJ $mole^{-1}$. Thus the results indicate that both processes have a role to play. It is interesting to note that the cold rolled titanium specimens show total immunity to SCC. The potential—time curve on unstressed cold rolled specimen (Fig. 2) clearly shows that passivation is almost instantaneous. Under stressed condition, even if the protective film breaks down, it gets repassivated immediately leaving no scope for the nucleation of stress corrosion cracks. Therefore the difficulty for stress corrosion crack initiation in cold rolled titanium specimens makes them

resistant to SCC. Hence the crack initiation process is the controlling factor in the SCC of the titanium specimens.

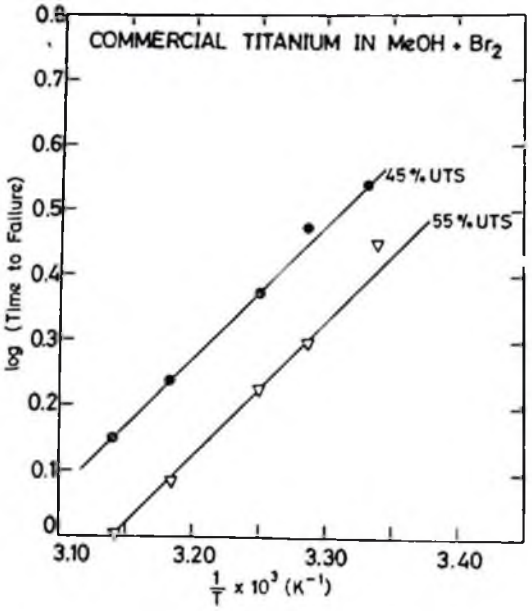


Fig. 6 ARRHENIUS PLOT OF TEMPERATURE DEPENDENCE OF TIME TO SCC FAILURE.

The crack initiation process depends on the applied stress as well as bromine concentration. The stress causes plastic deformation rupturing mechanically the passivating film and facilitates the halide ion diffusion to the base metal[13]. This consequently causes accelerated anodic dissolution. The stress accelerated dissolution process is clearly demonstrated by the increase in the weight loss at higher applied stress levels. The bromine concentration, which decides the diffusing halide ion concentration, also has a considerable effect on SCC life (Fig. 5). The presence of water beyond certain critical value (> 0.1 vol %) will lead to the formation of a surface passive film and enhances the SCC life. Once the stress corrosion cracks get initiated, the propagation process appears to be relatively easy and will have contributions from the halide ion diffusion to crack tip and anodic dissolution.

CONCLUSIONS

1. Commercial titanium undergoes intergranular corrosion in MeOH + Br_2 solution and shows SCC susceptibility when subjected simultaneously to tensile stress.

2. Cold rolling of titanium provides total immunity to SCC.

3. The activation energy for SCC is estimated to be 38.5 KJ $mole^{-1}$ which suggests a process of anodic dissolution.

4. The crack initiation is the rate controlling step in SCC and is facilitated by the diffusion of halide ions and the applied stress.

TABLE-1. Chemical Composition and Tensile Properties

Element	C	Fe	N	O	H
% Composition	0.022	0.07	0.014	0.14	0 01
	0.2% Y.S (MNm^{-2})		UTS (MNm^{-2})		% Elong
Tensile Properties					
a) Longitudinal	324		490		25
b) Transverse	338		462		26

TABLE-2. Heat treatment—Grain Size—Tensile properties

				($\dot{\epsilon}$ = 4.5 x 10^{-3} Sec^{-1}) TENSILE PROPERTIES.		
Heat treatment			Grain size μm	0.2% Y.S. MNm^{-2}	UTS MNm^{-2}	% Elong
1100 K,	28 hrs,	furnace cooled	117	356	495	30
,,	15	,,	105	320	520	31
,,	10	,,	76	336	505	35
,,	5	,,	60	353	505	37
,,	2	,,	51	338	440	29
1000	0.25	Air cooled	19	375	490	33
900	0.2	,,	11	390	530	34

TABLE-3. Tensile properties of annealed and cold rolled titanium before and after soaking

$\epsilon^{\circ} = 3.12 \times 10^{-3}$ Sec^{-1}

Test	0.2%YS (MNm^{-2})		UTS ($MNmO^{-2}$)		%Elong	
	Annealed	80% Cold Rolled	Annealed	80% Cold Rolled	Annealed	80% Cold Rolled
Tested in air	334	702	417	815	23.1	1.8
Soaked for 21 hours in the medium and tested in air.	294	695	405	825	1.8	1.7

TABLE-4. Influence of Grain size on time to SCC failure

Temp: 298 K	At 65% UTS						
Grain sizes μm	11	19	51	60	76	105	117
Time to failure, Hours.	2.90	2.75	2.10	1.55	1.10	0.65	0.30

REFERENCES

1. N.D. Tomashov, R.M. Altovskii and V.B. Vladimirov, Study of the corrosion of titanium and its alloys in methyl alcohol solutions of bromine. Translation FTD-TT-63-672/1+2, pp. 221-233, Translation Division, Foreign Technology Division WPAFB, Ohio.
2. K. Mori, A. Takamura and J. Shimose, Corrosion 22 (1966) 29-31.
3. E.G. Haney, R. Goldberg, R.E. Ernsberger and W.T. Brehm, Investigation of SCC of Ti alloys, Mellon Institute Progress Report No. 2 (NGR-39-008-014), May 1967, Mellon Institute, Pitsburg, Pa.
4. A.J. Sedriks, P.W. Slattery and E.N. Pugh, SCC of α—titanium in non-aqueous environments' Proceedings of the Int. Conf. on Fundamental aspects of SCC, Ohio State University, Sept. 1967.
5. A.J. Sedriks, DMIC Seminar on Accelerated crack propagation of titanium in methanol, halogenated hydrocarbons and other solutions, March 1967, DMIC memorandum 228, pp. 43-47.
6. A.J. Sedriks, J.A S. Green and P.W. Slattery, Corrrosion 24 (1968) 172-177.
7. A.J. Sedriks, and J.A.S. Green, Corrosion 25 (1969) 324-328.
8. M.J. Blackburn, J.A. Feeny and T.R. Beck, Part 4 of monograph review of the state-of-the-art of stress corrosion cracking in High Strength Steels, Titanium alloys and Aluminium alloys, Ed. B.F. Brown, U.S. Govt. Printing Office.
9. J. Spurrier and J.C. Scully, Corrosion 28 (1972) 453-463.
10. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Third Edition (1964) pp. 944, E.L.B.S and Longmans, Green & Co. Ltd.
11. M.J. Blackburn, J.A. Feeney and T.R. Beck in 'Advances in Corrosion Science and Technology' Vol. 3. Eds. M.G. Fontana and R.W. Staehle (1973) pp. 154, Plenum Press, New York.
12. C,M. Chen, H.B. Kirkpatrick, and H.L. Gegel, 'Stress Corrosion Cracking Mechanisms of Titanium and Its alloys', Atlanta, Georgia, January, 1971.
13. H.J. Engell in 'The Theory of Stress Corrosion Cracking in Alloys', Ed J.C. Scully, (NATO, 1971) pp, 86.

Asian Paints' Research and Development are more than surface deep

Equipped by one of the finest labs in the country, our technical research and development wing keeps in close touch with newest trends in surface coatings. Import substitution with indigenous materials has been a tradition with us.

Fundamental research on raw materials has resulted in putting to use unconventional materials available in India.

This costs the Company a few lakhs annually. But then we don't grudge the expense. Our research boys are doing so well there.

Projecting tomorrow's marketing needs, analysing the trends of consumer behaviour for this country's size, is a gigantic job. Professionals in the field keep the facts at fingertips. EDP facility makes the task easier.

Development of materials for mass markets is our commitment.



ANY SURFACE THAT NEEDS PAINTING
NEEDS asian paints

AIYARS-A. 178