

The Crevice Corrosion Resistance of Some Titanium Materials

A REVIEW OF THE BENEFICIAL EFFECTS OF PALLADIUM

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The crevice corrosion that occurs on titanium in chloride solutions at elevated temperatures can constitute a serious problem. The resistance of three titanium materials to this form of corrosion has been evaluated by immersion and electrochemical tests. The results show that all three possess superior corrosion resistance to that of commercially pure titanium, and that the two which contain palladium are the best. On the basis of these tests, mechanical properties and in-service experience, guide lines for the advantageous use of these materials are proposed.

It is well known that one of the important properties of titanium is its immunity to both pitting corrosion and stress corrosion cracking in chloride solution, an environment which causes corrosion of stainless steels. Consequently titanium is used extensively for vessels in the chemical industries, and for heat transfer tubes in steam turbine condensers and multi-stage flashing type desalination plants. However titanium can suffer from crevice corrosion in hot chloride solution, and as titanium is commonly used in such conditions this form of corrosion can constitute a practical problem.

For these reasons the effects of environmental factors such as chloride ion concentration, temperature, and the pH of the solution on crevice corrosion have already been investigated (1-4). Moreover, several methods of preventing crevice corrosion on titanium have been proposed, and some resistant materials have been developed. The most popular of these is titanium-0.15 per cent palladium (Ti-0.15Pd) (5). Currently titanium-0.3 per cent molybdenum-0.8 per cent nickel (Ti-0.3Mo-0.8Ni) is being investigated (6), because of its lower cost, while a mixture of palladium and titanium oxides (PdO/TiO₂-Ti) is being applied to industrial equipment by a simple surface treatment. In this paper the

crevice corrosion resistance of these three materials is compared with that of commercially pure titanium (C.P. Ti).

Evaluation of Materials

The test materials were in the form of sheet, 3 mm thick. Their chemical compositions are given in Table I. The procedure for coating titanium with palladium and titanium oxides has been reported previously (7). Methanol solution containing PdCl₂ and TiCl₃ was applied to the titanium, which had been prepared by sand blasting followed by pickling in hydrochloric acid. The surface was then oxidised to PdO and TiO₂ by heating in air for 10 minutes at a temperature of 600°C. The composition of the resulting coating was 70 molar per cent PdO and 30 molar per cent TiO₂, and the coating thickness 0.4 μm. Two types of specimen used for the immersion tests are shown in Figure 1. The multi-creviced specimen (a) was prepared by bolting two PTFE (Teflon) spacers, each having 16 grooves on the contacting face, to the titanium sheet by means of titanium fasteners (8). A measure of the occurrence of crevice corrosion in the metal/Teflon crevices was obtained by comparing the number of crevices which suffered corrosion with the total number of crevices, namely 32.

Table I									
Chemical Compositions of Test Materials									
Material	ASTM grade (B256)	Chemical composition, weight per cent							
		Fe	O ₂	N ₂	H ₂	Mo	Ni	Pd	Ti
C.P. Ti	G2	0.053	0.074	0.004	0.002	—	—	—	Bal.
Ti-0.3Mo-0.8Ni	G12	0.048	0.125	0.002	0.002	0.28	0.87	—	Bal.
Ti-0.15Pd	G7	0.046	0.081	0.003	0.003	—	—	0.16	Bal.

On the other hand, crevice corrosion in metal/metal crevices was determined using specimen (b), which consists of two titanium plates held together by titanium fasteners and Teflon spacers.

In addition, electrodes for electrochemical measurements were prepared by spot welding titanium lead wires onto specimen (b), or onto a piece of titanium sheet 15 mm × 20 mm. Apart from a 1 cm² test area, the surfaces were insulated with fluoric resin, and except for PdO/TiO₂-Ti, the test areas were polished with abrasive paper before measurements were made.

After the specimens had been immersed in various boiling chloride solutions for several hours a visual check was made for crevice corrosion. To determine the initiation of crevice attack, the corrosion potentials (E_{cor}) of the test electrodes were measured continuously while they were in boiling chloride solutions, and the times for the potentials to shift suddenly to the less noble side were recorded.

The occurrence of crevice attack on four different titanium materials/PTFE multi-creviced specimens, in boiling chloride solutions, is given in Table II. From this it is clear that the resistance of the two alloys and the coated sample was much superior to that of commercially pure titanium. The surface appearance of the commercial titanium after crevice corrosion attack is illustrated in Figure 2. The effect of the pH value on the occurrence of corrosion in a boiling 20 per cent sodium chloride solution is shown in Figure 3. The occurrence on commercial titanium increased with decreasing pH and

reached 80 per cent at pH 1.5. However in the pH range 6 to 2 the occurrence was zero for the other three materials, but at pH 1.5 the occurrence for the base metal alloy was 7 per cent. It is therefore suggested that the two palladium-containing materials were better than the other two in low pH solutions.

The variation in the corrosion potential of

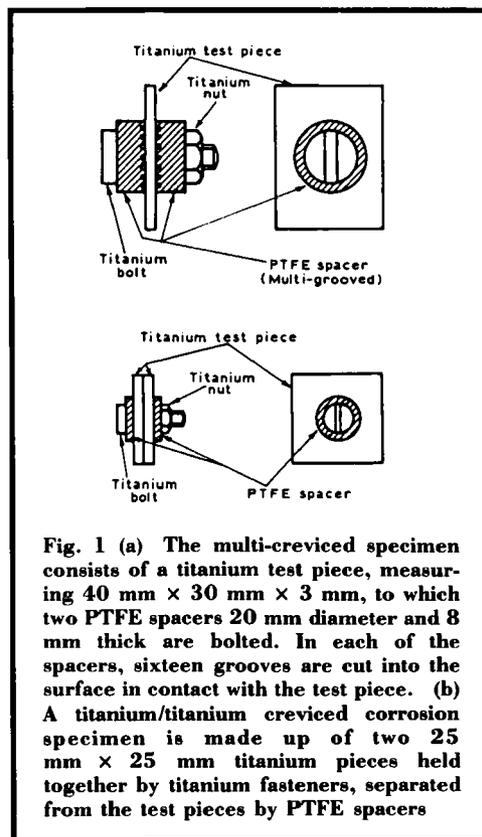


Fig. 1 (a) The multi-creviced specimen consists of a titanium test piece, measuring 40 mm × 30 mm × 3 mm, to which two PTFE spacers 20 mm diameter and 8 mm thick are bolted. In each of the spacers, sixteen grooves are cut into the surface in contact with the test piece. (b) A titanium/titanium creviced corrosion specimen is made up of two 25 mm × 25 mm titanium pieces held together by titanium fasteners, separated from the test pieces by PTFE spacers

commercial titanium and also of the Ti-0.3Mo-0.8Ni/PTFE-creviced electrodes with time in a boiling solution of 42 per cent magnesium chloride is shown in Figure 4. The E_{cor} of the former showed a noble potential of about $-0.4V$ at an early stage of immersion but the potential shifted abruptly to the less noble side after about 15 hours, and steadied at about $-0.6V$. After 48 hours corrosion was visible, see Figure 5. Additional tests have shown that there is a correlation between the abrupt change in the E_{cor} and the onset of crevice corrosion; thus it was established that the time to initiation of crevice corrosion was 15 hours for commercial titanium/PTFE-creviced specimens. However for the Ti-0.3Mo-0.8Ni/PTFE no abrupt change in the E_{cor} occurred, and no crevice corrosion was observed.

Using this technique, the time to initiation of the crevice attack on all four titanium materials was determined in boiling solutions of both sodium chloride and magnesium chloride; the results being given in Table III. In magnesium chloride, Ti-0.3Mo-0.8Ni/PTFE was subjected to attack after 168 hours, however no attack was observed on either of the palladium-containing materials, even after 240 hours. These results confirm the earlier findings of the immersion test.

The occurrence of crevice corrosion in titanium is attributable to Cl^- ion enrichment

Material	20%NaCl(pH4) 240 h	42%MgCl ₂ 48 h
	Occurrence of crevice attack, per cent	
C.P. Ti	13	56
Ti-0.3Mo-0.8Ni	0	0
Ti-0.15Pd	0	0
PdO/TiO ₂ -Ti	0	0

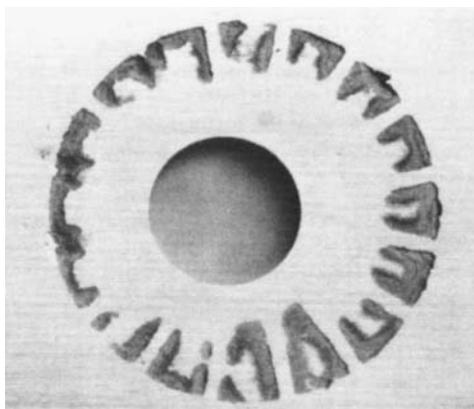


Fig. 2 After the immersion test for crevice corrosion, the surface of this commercially pure titanium shows the influence of the grooves cut into the contacting surface of the PTFE

and falling pH of the solution present in the crevice; this is followed by active dissolution of titanium in the crevice due to the breakdown of the passive film (9). As crevice corrosion resistance depends upon the maintenance of the passive state it is necessary to determine the critical hydrochloric acid concentration for depassivation. In this study sodium chloride

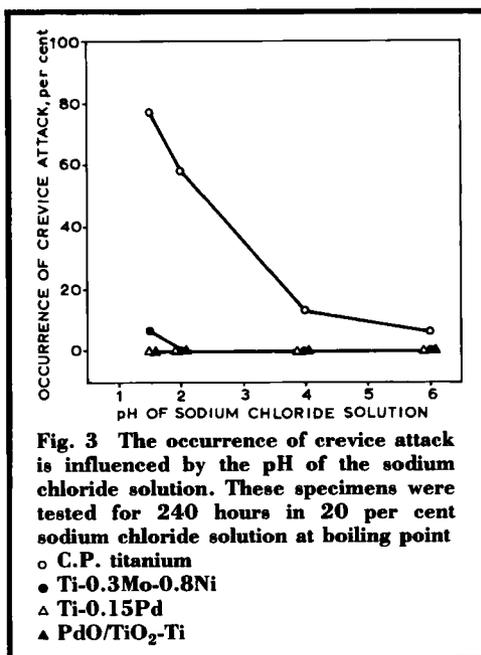
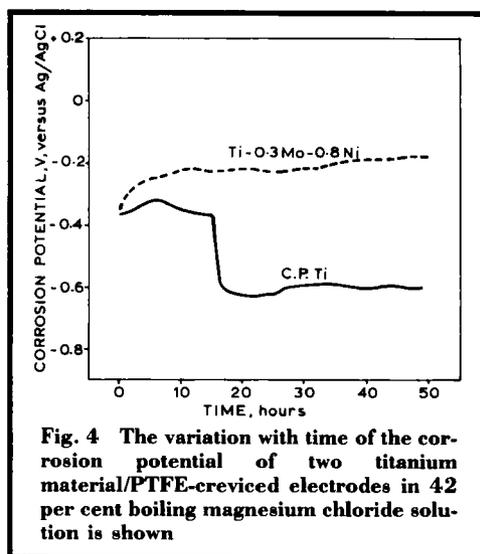


Fig. 3 The occurrence of crevice attack is influenced by the pH of the sodium chloride solution. These specimens were tested for 240 hours in 20 per cent sodium chloride solution at boiling point
 ○ C.P. titanium
 ● Ti-0.3Mo-0.8Ni
 △ Ti-0.15Pd
 ▲ PdO/TiO₂-Ti

Table III Time to Initiation of Crevice Attack for Titanium Materials in Boiling Chloride Solutions (Ti/PTFE-creviced electrode)			
Material	6%NaCl (pH6)	20%NaCl (pH4)	42%MgCl ₂
	Time to initiation of crevice attack, hours		
C.P. Ti	220	92	15
Ti-0.3Mo-0.8Ni	>720	>720	168
Ti-0.15Pd	>720	>720	>240
PdO/TiO ₂ -Ti	>720	>720	>240

solution containing hydrochloric acid was used as the model solution.

Typical test results are given in Figure 6. Commercially pure titanium has a passive state potential up to 0.06M hydrochloric acid concentration, but the E_{cor} shifts abruptly to the less noble side at 0.08M, and steadies at approximately $-0.7V$ indicating the active state. This suggests that the critical hydrochloric acid concentration, for depassivation of commercial titanium is 0.07M. The results found for



Ti-0.3Mo-0.8Ni, PdO/TiO₂-Ti and Ti-0.15Pd were 0.8, 1.3 and 1.4M, respectively.

The effect of solution temperature on the critical hydrochloric acid concentration is shown in Figure 7, where it is evident that the critical concentration for each of the materials decreases with increasing temperature. Thus:

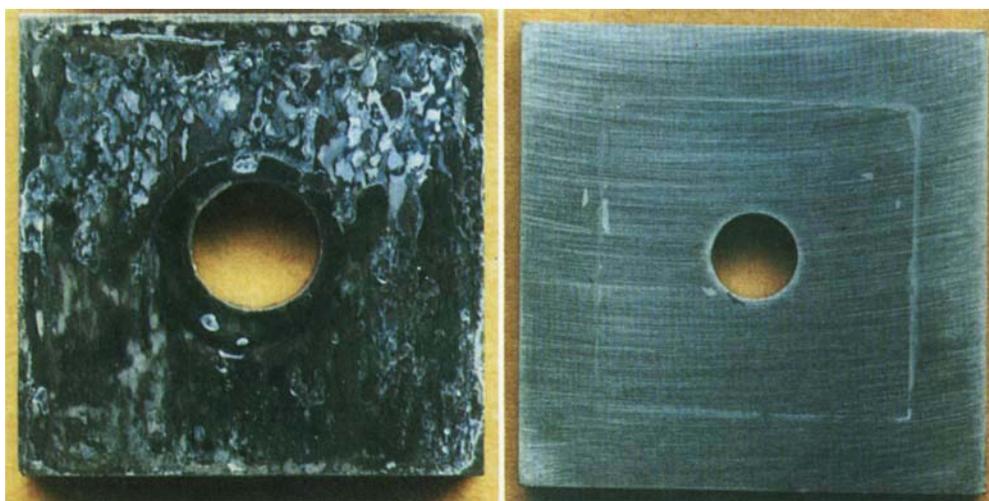
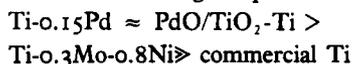


Fig. 5 After 48 hours in a boiling solution of 42 per cent magnesium chloride this C.P. titanium/PTFE-creviced specimen (left) shows corrosion of the surface, while the surface of Ti-0.15Pd/PTFE-creviced specimen after the test shows immunity from crevice corrosion (right)

The ability to maintain the passive state is highest for PdO/TiO₂-Ti and Ti-0.15Pd, and this correlates with an excellent resistance to crevice corrosion.

In order to discuss the crevice corrosion resistance of the four test materials, anodic and

cathodic polarisation curves were measured in boiling 1M sodium chloride + 1M hydrochloric acid solutions. The test results are presented in Figure 8. The E_{cor} of commercial titanium was -0.67V, and a high current peak corresponding to active dissolution was observed in the anodic

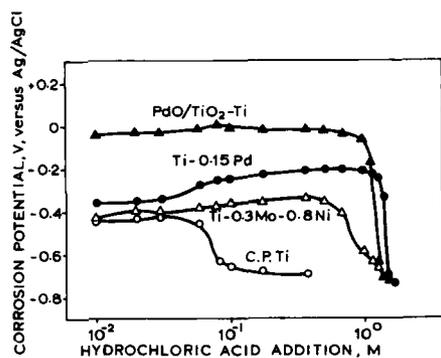


Fig. 6 The corrosion potentials of four titanium materials in boiling 1M sodium chloride solution are shown to vary with hydrochloric acid addition (free-surface electrode)

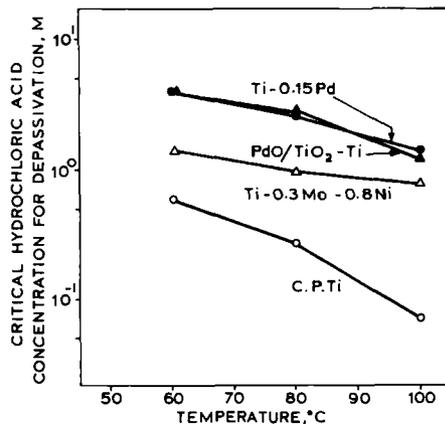


Fig. 7 The influence of temperature upon the critical hydrochloric acid concentration for the depassivation of four titanium materials in deaerated 1M sodium chloride solution is shown. For each material the critical concentration decreases with increasing temperature

Fig. 8 Polarisation curves are shown for four titanium materials in boiling 1M sodium chloride with 1M hydrochloric acid. The corrosion potentials of both Ti-0.15Pd and PdO/TiO₂-Ti, where no anodic peaks occur, are more noble than those of C.P. titanium and Ti-0.3Mo-0.8Ni

- C.P. titanium
- Ti-0.3Mo-0.8Ni
- △ Ti-0.15Pd
- ▲ PdO/TiO₂-Ti

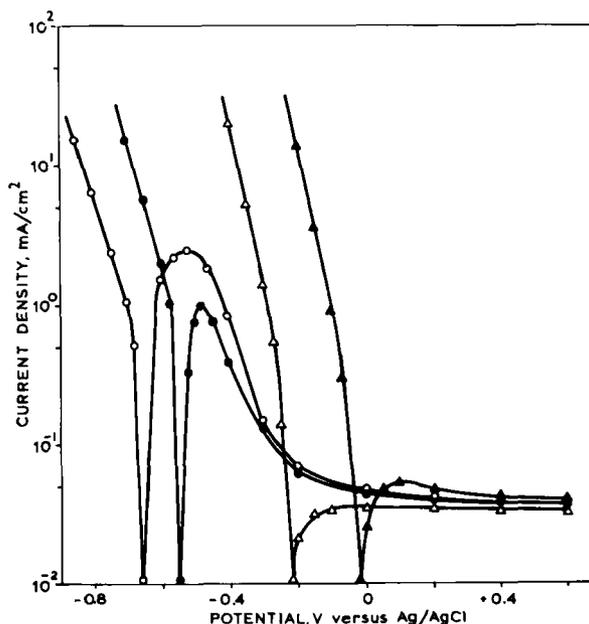


Table IV Result of Crevice Corrosion Test for Crevice Specimens in Boiling 20 per cent Sodium Chloride Solution of pH4 for 240 hours		
Crevice specimen assembly	Occurrence of crevice attack	
	Coupled Ti C.P. Ti	material
C.P. Ti with C.P. Ti	Severe	Severe
C.P. Ti with Ti-0.3Mo-0.8Ni	Slight	None
C.P. Ti with Ti-0.15Pd	None	None
C.P. Ti with PdO/TiO ₂ -Ti	None	None

polarisation curve. For Ti-0.3Mo-0.8Ni, E_{cor} was $-0.55V$ which was more noble than that of commercial titanium and the anodic current peak and cathodic polarisation were lower than that of commercial titanium. Consequently it can be considered that the corrosion resistance of this material is improved by suppressing anodic dissolution and decreasing cathodic polarisation. In contrast, the corrosion potential of Ti-0.15Pd and PdO/TiO₂-Ti were more noble than those of the other two materials and no anodic peaks were observed. These phenomena were attributable to enrichment of the Ti-0.15Pd surface with metallic palladium (10) and to the low hydrogen overvoltage of the palladium and PdO/TiO₂ films; which explains

Table V Effective Application of Crevice-Corrosion-Resistant Titanium Materials			
Material	Situations where Maximum Advantage is Gained		
	Mechanical conditions	Chemical Environment	Remarks
Ti-0.3Mo-0.8Ni	Fixed or changing, can withstand abrasion	Only slightly aggressive	High-temperature strength
Ti-0.15Pd	Fixed or changing, can withstand abrasion	Aggressive	Excellent service performance
PdO/TiO ₂ -Ti	Fixed, abrasion must be avoided	Aggressive	Coating is simple to apply

Table VI Typical Examples of Industrial Application of Crevice-Corrosion-Resistant Titanium Materials				
Material	Application		Service conditions (possibility of crevice corrosion in C.P. Ti)	Condition in the crevice
	Process	Equipment		
Ti-0.3Mo-0.8Ni	Oil refinery	Shell and tube heat exchanger	Hydrocarbon + Cl ⁻ 90 ~ 170 °C (Critical)	Not fixed, scale is deposited
Ti-0.15Pd	Salt purification	Concentrator	Cl ⁻ ≈ 20%, pH2 120 ~ 130 °C (Probable)	Not fixed, salt is deposited
PdO/TiO ₂ -Ti	Fertiliser	Mono-tube heat exchanger	Cl ⁻ ≈ 30%, pH5 130 ~ 140 °C (Possible)	Fixed at the flange/gasket junction

why these two materials show such excellent resistance to crevice corrosion.

In chemical equipment, such as heat exchangers and reactors, crevices may occur between commercial titanium and dissimilar titanium materials. For example when commercial titanium and Ti-0.15Pd are used as tube and tube plate materials, respectively, in a heat exchanger crevices occur at the junctions of the tubes and the plates. In such situations the restraining effect of the Ti-0.15Pd against the corrosion of the commercially pure titanium is of considerable practical importance. For this reason, immersion tests on creviced specimens of commercial titanium/dissimilar titanium material were carried out in boiling 20 per cent sodium chloride solution (of pH 4). For commercial titanium coupled with Ti-0.15Pd or PdO/TiO₂-Ti no crevice corrosion was observed, however commercial titanium coupled with Ti-0.3Mo-0.8Ni showed slight corrosion of the commercially pure titanium although the Ti-0.3Mo-0.8Ni was immune, as shown in Table IV. The results also show that the two palladium containing materials were superior to Ti-0.3Mo-0.8Ni for preventing crevice corrosion of the commercial titanium.

Differences exist amongst the titanium materials evaluated; the main features being summarised in Table V.

Although the corrosion resistance of Ti-0.3Mo-0.8Ni is better than that of commercially pure titanium, it is inferior to both Ti-0.15Pd and PdO/TiO₂-Ti. It has good mechanical properties at elevated temperatures enabling it to be used in more highly stressed designs than commercial titanium (11). In addition it is less expensive than Ti-0.15Pd.

Titanium-0.15 per cent palladium has the best resistance to corrosion and it has been used in actual equipment for periods of 20 to 25 years without any serious crevice corrosion problems. Therefore it is recommended for use in severely corrosive environments when high reliability against crevice corrosion is necessary.

The third material is not homogeneous, but a composite of commercial titanium protected against corrosion by a thin coating of oxides.

Because this coating is simple to apply, fabricated components as well as plate, wire and tube can be treated. The corrosion resistance of coated material is the same as that of Ti-0.15Pd, but because the coating is thin degradation by mechanical erosion, which could be caused by flowing liquids, must be avoided. One application for this coating is for the flanges of reactors and for the joints of tubes and tube plates in heat exchangers.

Typical industrial applications of the titanium materials which are resistant to crevice corrosion are listed in Table VI.

Conclusion

The crevice corrosion resistances of titanium-0.3 per cent molybdenum-0.8 per cent nickel, titanium-0.15 per cent palladium and titanium coated with a mixture of palladium and titanium oxides have been evaluated and guide lines for the optimum use of these materials are proposed, on the basis of their resistance to corrosion, their mechanical properties and on in-service industrial experience. If these factors are taken into account then titanium materials can be used effectively, without crevice corrosion.

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