

The Role of Palladium in Enhancing Corrosion Resistance of Titanium

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It is well known that the addition of about 0.2 per cent palladium to titanium significantly increases its resistance to corrosion in non-oxidising acids. It has usually been assumed that the palladium is present as elemental particles at the metal surface and that these function electrochemically to provide anodic passivation of the titanium matrix. It has, however, now been demonstrated that even in low concentration palladium additions to titanium form Ti_2Pd , and that before onset of passivation the palladium dissolves in the corrodent and is then reprecipitated in elemental form from solution. This process is accompanied by the growth of a protective film of TiO_2 . In substantiation of this mechanism it can be shown that corrosion of unalloyed titanium in non-oxidising acids can be halted by the addition to the acid of a very small quantity of a soluble palladium salt.

The increase in resistance to corrosion in non-oxidising acids conferred upon titanium by a small alloying addition of noble metal has been known for about seven years (1). Theory predicts that anodic passivation of the titanium matrix will be achieved once sufficient noble metal has concentrated at the surface to provide the requisite galvanic exchange current to elevate the titanium potential above a critical value.

Protection is usually only achieved after an initial induction period during which a fairly

high rate of corrosion is observed, and this is then succeeded by a very significant reduction in the corrosion rate. In the early work on titanium-palladium alloys it was thought that during this induction period preferential solution of titanium took place, that when sufficient metallic palladium was available at the metal surface the anodic passivation mechanism followed, and that this resulted in the diminution of the corrosion rate.

There was, however, some doubt as to the form in which titanium was present in titanium-palladium alloys and further investigation has now shown that even at a concentration as low as 0.15 wt per cent the palladium is present as Ti_2Pd . Fig. 1 shows the presence of an elongated Ti_2Pd phase in the Ti-0.15 per cent Pd alloy at a magnification of 55,000.

Palladium present in the titanium matrix as Ti_2Pd clearly will not have the electro-



Fig. 1 The structure of a titanium-0.15 per cent palladium alloy showing elongated particles of a Ti_2Pd phase ($\times 55,000$)

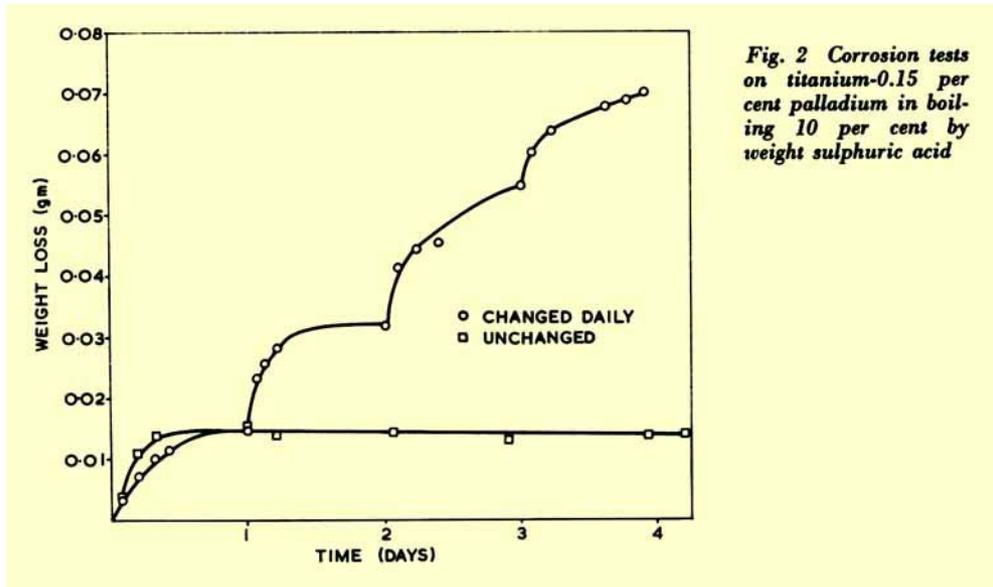


Fig. 2 Corrosion tests on titanium-0.15 per cent palladium in boiling 10 per cent by weight sulphuric acid

chemical properties attributable to metallic palladium and it is necessary to seek an alternative explanation for the mechanism by which the alloy functions.

Corrosion tests in which coupons of titanium-0.15 per cent palladium are exposed to boiling 10 wt per cent sulphuric acid under stagnant and replenished conditions, provide an indication of the mechanism involved. In stagnant conditions there is an induction period of about 20 hours of rapid corrosion, succeeded by almost com-

plete cessation of corrosion. If, however, the acid is replenished at daily intervals, successive increments in the amount of corrosion are recorded after each replenishment, and there is no permanent passivity, as shown in the graph of Fig. 2.

Analysis of the acid at the onset of passivity shows that at this point the bulk liquor contains about 0.9 parts per million of palladium.

This suggests that initially the Ti_2Pd phase as well as the matrix titanium suffers dissolution, and that when a sufficient con-

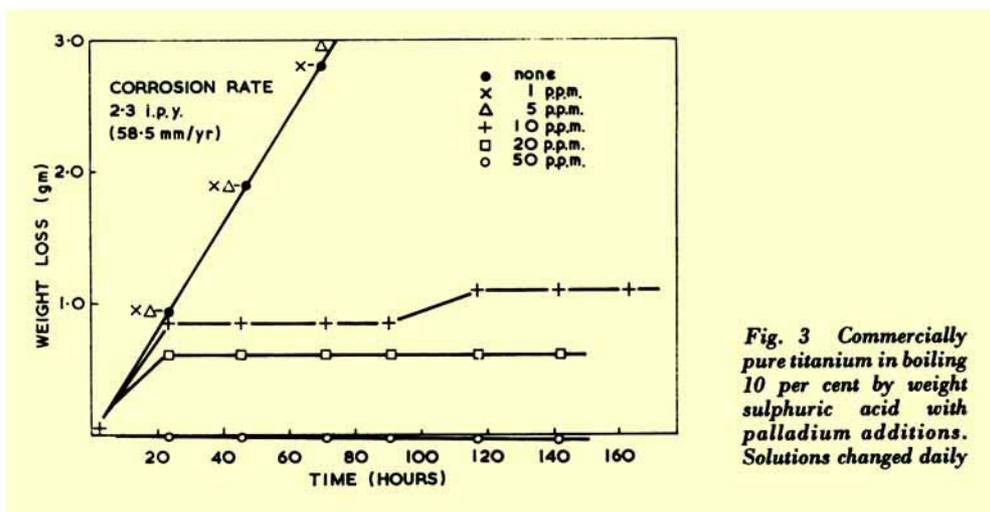


Fig. 3 Commercially pure titanium in boiling 10 per cent by weight sulphuric acid with palladium additions. Solutions changed daily

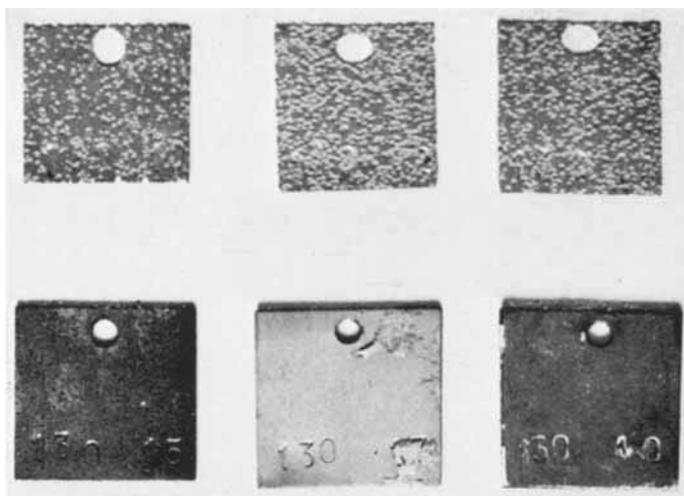


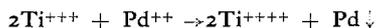
Fig. 4 Specimens of commercially pure titanium in boiling 10 per cent by weight sulphuric acid with palladium additions
 Top, left to right
 0, 1, 5 p.p.m. palladium
 Bottom, left to right
 10, 20, 50 p.p.m. palladium

centration of palladium ions has built up in solution metallic palladium is precipitated at the metal surface. This could then bring into play the anodic passivation mechanism suggested by Stern and Bishop (1) and Cotton (2, 3). The induction period of rapid corrosion is necessary in order to build up the required soluble palladium. There is confirmation of this in that if the amount of alloying palladium in the alloy is increased from 0.15 to 0.5 per cent, the induction period virtually disappears, presumably because the appropriate concentration of soluble palladium builds up much more rapidly.

Further confirmation of this mechanism is obtained if unalloyed titanium is exposed to 10 wt per cent boiling sulphuric acid to which palladium chloride is added to provide incremental amounts of soluble palladium at levels from 1 to 50 p.p.m., the liquor being changed daily. Results, illustrated graphically in Fig. 3, show that onset of passivity takes place when the concentration of soluble palladium reaches about 10 p.p.m. This is a considerably higher palladium level than that detected in the bulk liquor resulting from initial dissolution of the titanium-palladium alloy, but this could be accounted for by the establishment of a concentration gradient in a thin layer of stagnant liquor at the surface of the alloy specimens.

At the 20 p.p.m. soluble palladium level there is visible evidence of the precipitation of metallic palladium at the titanium surface, but at a concentration of 50 p.p.m. a dark oxide film is formed, presumably containing some palladium, and a continuing slow weight increase is observed.

A protective film of titanium oxide could result from oxidation of soluble titanium followed by a precipitation process. Thus when the titanium initially corrodes it passes into solution as Ti^{+++} and this will be oxidised by Pd^{++} according to the reaction



Ti^{++++} is unstable and precipitates as TiO_2 .

This is a somewhat different concept of what is regarded as the normal anodic passivation of metallic titanium that is presumed to take place on the metal surface and it is probable that both mechanisms are involved in the growth of protective films on titanium-palladium.

References

- 1 Milton Stern and Claude B. Bishop, *Trans. A.S.M.* 1960, 52, 239-256; see also *Platinum Metals Rev.*, 1959, 3, 88-89
- 2 J. B. Cotton, *Chemistry & Industry*, 1958, 68-69 and 492-493
- 3 J. B. Cotton, *Werkstoffe und Korrosion*, 1960, 11, 152-155