

Increasing the Resistance of Titanium to Non-Oxidising Acids

INFLUENCE OF ADDITIONS OF PLATINUM METALS

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A recent article in this journal (1) summarised some of the work of Tomashov and his colleagues in the course of which the influence of small additions of platinum metals to 18-8 type stainless steels on their resistance to acids was explored. In that article it was suggested that "the general principle of alloying with small quantities of noble metals may find use in further increasing the passivity of metals such as titanium, zirconium and tantalum towards acids". An abstract of a paper (in Japanese) by Nishimura and Hiramatsu (2) appeared in the same issue of *Platinum Metals Review*; this reported, *inter alia*, the beneficial effect of 2 per cent additions of platinum or palladium in reducing the corrosion rate of titanium in 20 per cent hydrochloric acid at 25°C. Moreover, Buck and Leidheiser (3) showed that the corrosion rate of titanium in boiling 2M hydrochloric acid is strikingly reduced by contact with platinum, palladium, rhodium or iridium—in contrast to the great increase of corrosion rate that such contact produces on most of the common metals.

The electrochemical behaviour of titanium in non-oxidising acids and the great improvement in its passivation effected by small additions of platinum metals has now been further studied by Stern and his colleagues at the Metals Research Laboratories of Union Carbide Metals Company. A preliminary note on this work has appeared in this journal (4); the present account is a review of three of their papers (5, 6, 7).

Stern and Wissenberg (5) examined the

general corrosion and passivation behaviour of titanium in sulphuric and hydrochloric acids of various concentrations at various temperatures. Fig. 1 is typical of the potential/external-current-density plots obtained potentiostatically. At very negative potentials, the plot substantially represents *cathodic* evolution of hydrogen. Near the "corrosion potential" (no external current) of -0.71 V (saturated calomel electrode scale), the plot represents the difference between the cathodic current and the anodic current equivalent to dissolution of titanium to soluble ions; Fig. 2 is an expanded view of this region, also showing how the corrosion current-

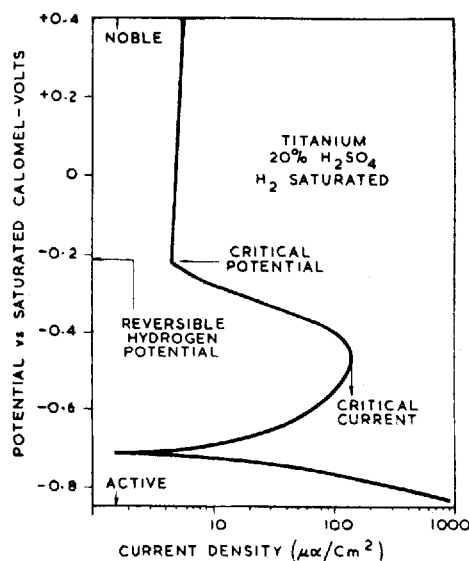


Fig. 1 Anodic and cathodic behaviour of titanium in hydrogen-saturated 20 per cent sulphuric acid at room temperature (Stern and Wissenberg)

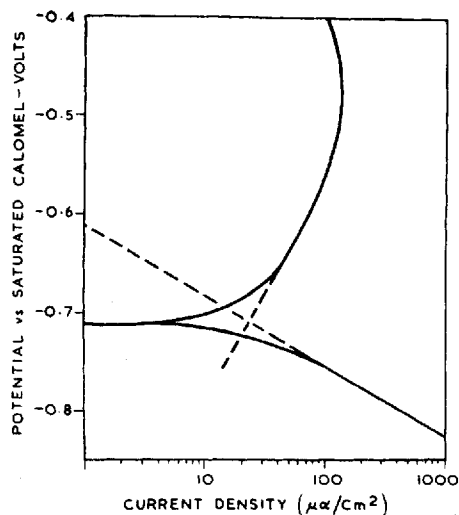


Fig. 2 Expanded view of part of Fig. 1, showing the calculated anodic polarisation curve of titanium

density can be obtained by extrapolation of the appropriate all-cathodic and all-anodic parts of the potential/external-current-density curve. At a critical anode current density, passivation begins, because at the corresponding potential, -0.48 V (sce) the production of insoluble titanium dioxide becomes thermodynamically possible. In Fig. 1, the authors label the top end of the unstable portion (decreasing current with increasingly positive potential) of the curve as a "critical potential". This potential probably has less significance than the potential above which the current *begins* to decrease, -0.48 V (sce); this latter value agrees closely with that to be expected for the onset of titanium dioxide formation in 20 per cent sulphuric acid, as indicated by the thermodynamic data collected and interpreted in the potential/pH diagrams of Schmets and Pourbaix (8). It is likely that with very slow experimental increase of potential, the authors' "critical potential" would be much lower and approximate to that at which the current *begins* to decrease. In any case, Stern and Wissenberg point out that since passivation due to oxide formation sets in at potentials more negative than the reversible hydrogen potential, passivation would be automatic if the rate

of the cathode reaction $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$ were large at but slight overpotential. However, as shown by the lowest part of the plot in Fig. 1, an overpotential of more than 0.5 V is required to give a cathode current density of $100\text{--}200 \mu\text{A}/\text{cm}^2$, necessary if the anode is to achieve passivation conditions, and consequently plain titanium is active and corrodes.

The modern general theory of passivation is given in detail elsewhere (9) but here the matter may be clarified by a schematic diagram, Fig. 3. Here ABCD is the anodic polarisation curve for the metal (AB active, BC passivating, CD passive). L is the reversible hydrogen potential, more positive than the passivating region BC, and LMN represents a cathode reaction that is rapid at small overpotential; the mixed potential M, and passivation of the metal, would be achieved. But actually the cathode reaction on unalloyed titanium requires considerable overpotential, LOP, and the mixed potential O, with corrosion, is observed.

Evidently, coupling the titanium anode with an auxiliary cathode of low overpotential, able to sustain current densities

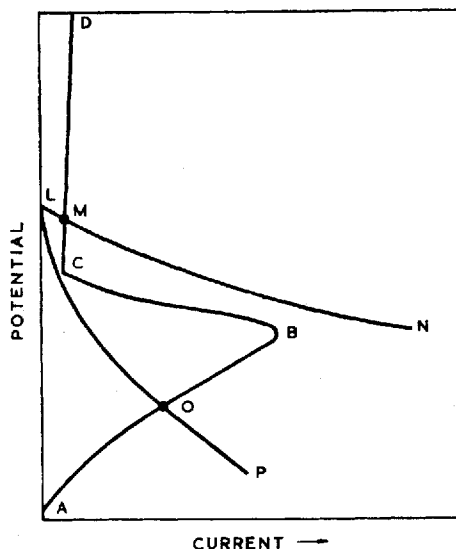


Fig. 3 Schematic diagrams showing passive (M) and active (O) mixed potentials

according to LMN, should produce passivation, and this is the explanation of the results of Buck and Leidheiser (3). Stern and Wissenberg (5) coupled several metals with titanium, obtaining the results given in Table I, which extend those of Buck and Leidheiser. All the metals tested could passivate titanium if sufficient area were present. Further potentiostat experiments with plain titanium (5) showed that, naturally enough, passivation becomes progressively more difficult as the temperature is increased and as the corrosive environment becomes more severe by increase of acid concentration. None the less, potentiostat curves similar to that of Fig. 1, with the passivating portion more negative than the reversible hydrogen potential, were obtained even in 10 per cent hydrochloric acid and 5 per cent sulphuric acid at the boiling points, indicating that passivation by

Couple	Area Ratio A (Ti) A (Cathode)	Weight Loss of Titanium (mg/dm ² /day)		
		Boiling 1% H ₂ SO ₄	Boiling 3% H ₂ SO ₄ + 5% Na ₂ SO ₄	Boiling 5% H ₂ SO ₄ + 5% Na ₂ SO ₄
Titanium ..	—	1,400	1,800	2,900
Titanium-18-8 Stainless ..	1	0		
	2	10		
	6.6	6		
Titanium-Hastelloy alloy F ..	1	0		
	12	2		
Titanium-Carbon	0.2	0	0	3,600
	0.5		0	
	1		1,200	
Titanium-Platinum	0.25			21
	1			65
	2			65
	4			108
	35			1,700

a low overpotential cathode is even here a possibility.

Stern and Wissenberg (6) next prepared alloys of titanium with small amounts of noble metals, so that points of low hydrogen overpotential should be present on the alloy surface. Table II gives some results. The

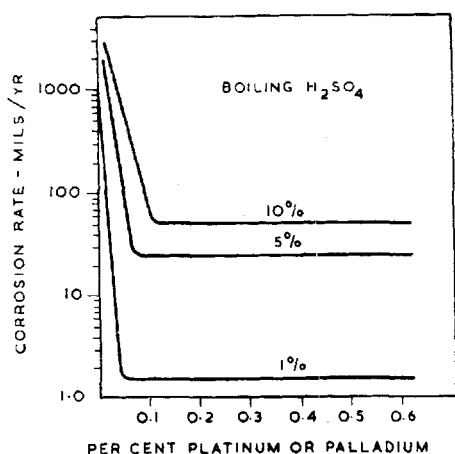


Fig. 4 Effects of platinum and palladium additions on the corrosion rate of titanium in boiling sulphuric acid solutions (Stern and Wissenberg)

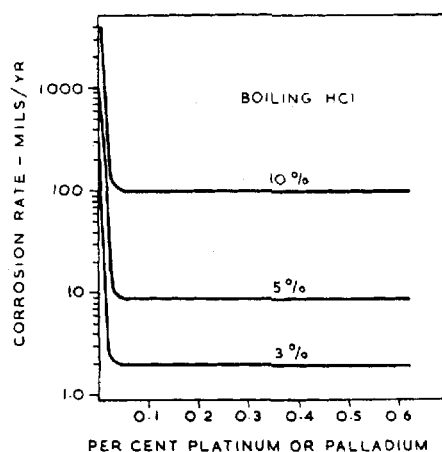


Fig. 5 Effects of platinum and palladium additions on the corrosion rate of titanium in boiling hydrochloric acid solutions (Stern and Wissenberg)

TABLE II
Effect of Various Alloy Additions
on the Corrosion Resistance of Titanium

Composition	Weight Loss in 24 Hours (Mils/Year)			
	Boiling H ₂ SO ₄		Boiling HCl	
	1%	10%	3%	10%
Titanium	460	3,950	242	4,500
Ti+0.064% Pt	<2	145	<2	128
Ti+0.54% Pt	<2	48	3	120
Ti+0.08% Pd	<2	166	3	100
Ti+0.44% Pd	<2	45	<2	67
Ti+0.1% Rh	<2	26	5	96
Ti-0.5% Rh	3	48	<2	55
Ti+0.1% Ru	3	187	5	280
Ti+0.5% Ru	<2	48	<2	113
Ti+0.11% Ir	<2	359	3	120
Ti+0.60% Ir	<2	45	3	88
Ti+0.10% Os	5	480	3	1,820
Ti+0.48% Os	<2	82	3	208
Ti+0.11% Re	235	—	345	—
Ti+0.36% Re	9	—	30	—
Ti+0.11% Au	1,050	—	1,500	—
Ti+0.48% Au	3	—	9	146
Ti+0.04% Ag	500	—	334	—
Ti+0.34% Ag	—	—	—	4,850
Ti+0.17% Cu	470	—	340	—
Ti+0.44% Cu	660	—	550	—

small additions of all six platinum metals are seen to give striking improvements in corrosion resistance even in hot and fairly concentrated sulphuric and hydrochloric acids. Platinum, palladium, rhodium and ruthenium gave the best results, osmium and iridium appearing to be slightly less effective. Similar additions of rhenium, gold, silver and copper give either a smaller improvement, or an actual increase of corrosion rate, doubtless because they are less effective cathodes, with higher overpotentials; in fact, the order of merit as passivators of the various metals examined was approximately the order of the exchange current for the reaction $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$ on their surfaces.

The points of low hydrogen overpotential

do not result from dissolution and redeposition of the noble metal, as shown by Stern and Bishop (7); titanium and titanium-palladium alloy corrode at their usual relatively fast and relatively slow rates even when they are together in the same vessel. The points of low hydrogen overpotential are therefore present on the alloy surface before any attack begins, or are produced during an induction period during which some titanium dissolves and exposes them.

Platinum and palladium additions were further investigated (6); Figs. 4 and 5 show the influence of platinum and of palladium content on corrosion rates in boiling sulphuric and hydrochloric acids of various concentrations. It is evident that the maximum benefit

to be derived from platinum metal additions is reached at quite small contents, of the order of 0.1 per cent—somewhat smaller for hydrochloric acid than for sulphuric acid conditions. The data of Figs. 4 and 5 are derived from 24-hour corrosion tests, and it is likely that active conditions at first prevailed in the alloys with the lower noble metal contents, until sufficient noble metal became exposed to give the requisite amount of cathodic stimulation to produce passivation; Fig. 6 shows potential/time curves that illustrate the effect.

Further experiments by Stern and Wissenberg (6) confirmed that the behaviour of titanium alloyed with platinum metals is as excellent as that of unalloyed titanium in oxidising acids. In non-oxidising acids saturated with oxygen, the alloys are decidedly better, because the somewhat uncertain passivating action of oxygen as a cathodic reactant is greatly enhanced.

Large Scale Experiments

The above results were sufficiently encouraging for Stern and Bishop (7) to examine titanium alloyed with palladium on a larger scale. Palladium was chosen as among the most effective, and as the least expensive, of the noble metals. A content of 0.22 per cent palladium was aimed at, as an ample excess over the 0.1 per cent previously

shown to give the maximal effect, and was achieved with very little segregation in an ingot 10 inches high and 4 inches in diameter by consumable arc melting of compacted titanium sponge and palladium powder. The ingot was hot-forged into slab and hot-rolled to 0.06 inch thick sheet; the fabricating properties of the alloy and the tensile properties of the sheet appeared to be identical with those of unalloyed titanium.

In oxidising media, the corrosion resistance of the alloy was as good as that of unalloyed titanium; it is obviously important that a new alloy should not show the excellent resistance of the unalloyed metal impaired under any conditions. The great improvement effected by palladium alloying for non-oxidising media is illustrated by the results given in Table III for seven acid media.

In a series of autoclave corrosion tests conducted at 190°C in various concentrations of hydrochloric and sulphuric acid, while unalloyed titanium, in the absence of oxidising agents, was rapidly attacked, the palladium alloy showed useful resistance in solutions containing up to 5 per cent of either acid.

On the basis of these and many other experiments, Stern and Bishop conclude that titanium—0.2 per cent-palladium alloy is second only to tantalum as a corrosion-resistant material able to handle strongly acid media that are either oxidising, non-

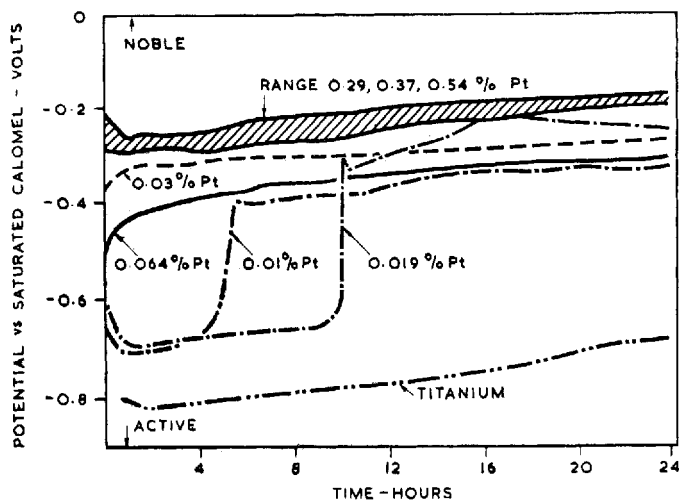


Fig. 6 Potential as a function of time for titanium, alloyed with various concentrations of platinum, in boiling 1 per cent sulphuric acid (Stern and Wissenberg)

TABLE III
Comparison of the Corrosion Resistance of Titanium-Palladium Alloy with Commercially Pure Titanium in Various Non-Oxidising Type Media

Environment	Corrosion Rate—Mils/Year	
	Commercially Pure Titanium	Titanium-Palladium Alloy
Aluminium chloride, 10%, boiling	<1	<1
Aluminium chloride, 25%, boiling	2020	1
Citric acid, 50%, boiling	17	<1
Formic acid, 50%, boiling	143	3
Hydrochloric acid, 5%, boiling	1120	7
Oxalic acid, 1%, boiling	1800	45
Phosphoric acid, 50%, aerated, 70°C	405	71
Phosphoric acid, 10%, boiling	439	127
Sulphuric acid, 5%, boiling	1920	20

oxidising or reducing, or which fluctuate in these respects. It is superior to titanium in being as good in oxidising and much better in non-oxidising and reducing acids; it is superior to zirconium in being at least as good in non-oxidising and reducing acids, and much better under oxidising conditions (which are inimical towards zirconium).

Whereas the practicability of platinum metal additions to stainless steels, as previously discussed (1), remains problematical, that of the same additions to titanium seems

to be scarcely in doubt. Not only is the passivating effect much more definite in the case of titanium; it is achievable most readily with the cheapest platinum group metal, palladium, and on a basic material that is, and no doubt will continue to be, considerably more expensive than stainless steel. It has been estimated that the addition of 0.1 per cent of palladium to titanium would add only something like 32 cents per lb, a very small fraction of the present or the foreseeable cost of titanium.

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