An Improved Titanium Alloy for Chemical Plant

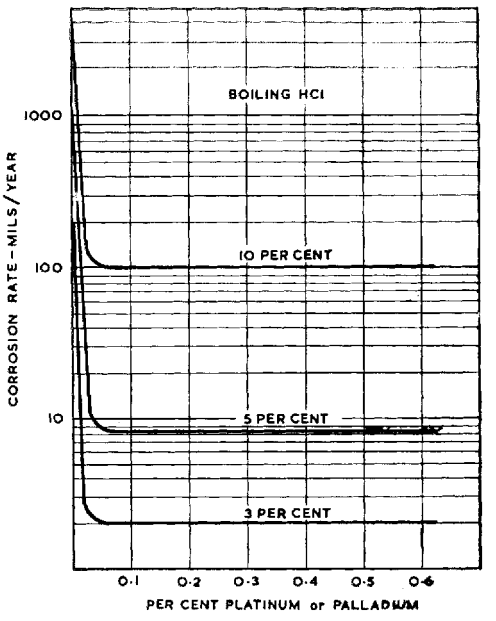
PALLADIUM ADDITION INCREASES RESISTANCE TO CORROSION

Although titanium has been widely used in the manufacture of chemical plant to withstand strongly oxidising conditions such as boiling nitric acid, it is not suitable for use in reducing environments such as hydrochloric and sulphuric acids. A recent discovery by the Union Carbide Metals Company means that it should now be possible to use titanium for applications requiring resistance to both oxidising and reducing conditions. Dr. Milton Stern, of the Company's Metals Research Laboratories, has found that the addition of as little as 0.1 per cent palladium to titanium renders the latter practically completely resistant to attack by boiling solutions of reducing acids.

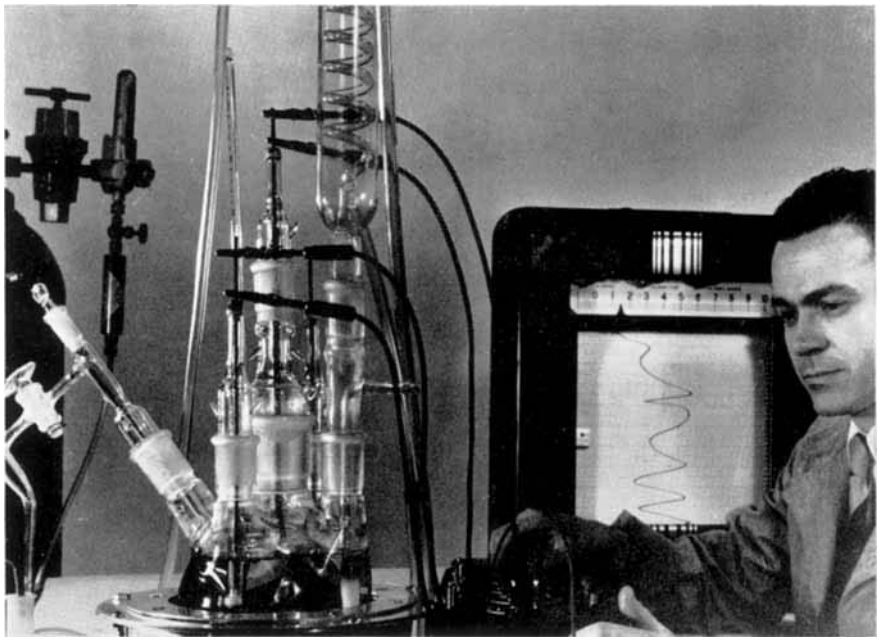
The effect of the palladium addition is explained by the electrochemical theory of corrosion and passivation of metals in solution. The theory has been outlined in a previous edition of this publication in a review of work by N. D. Tomashov and his colleagues on additions of platinum and palladium to stainless steels (*Platinum Metals Review*, 1958, **2** (4), 117–119).

A metal in solution is considered to be passive when it is covered by a stable film of oxide. The condition that this oxide layer should be stable is that the potential of the metal surface is more positive than the limiting value at which formation of oxide occurs in preference to formation of a soluble corrosion product. The necessary increase in potential can be brought about electrochemically, by making the metal an anode in the solution, or chemically, by the presence in solution of some reactant which raises the metal potential by rapid cathodic reduction on its surface. For titanium, and many other metals such as iron and steel, nitric acid is such a reactant and causes passivation of the metal surface. Titanium in fact has such a low critical potential for oxide formation that it is very easily passivated and it is only in strongly reducing solutions that it is reactive due to its low exchange current for the hydrogen-ion reduction reaction.

As was demonstrated by Tomashov for stainless steels, and is now extended to titanium by Dr. Stern, a metal can be passivated in a third way, by alloying with small amounts of a noble metal which is resistant to the solution under consideration. In the case of titanium the relevant solutions



Effect of platinum and palladium additions to titanium on rate of corrosion in various concentrations of boiling hydrochloric acid



Electrochemical apparatus used in the Metals Research Laboratories of Union Carbide Metals Company in obtaining data on the dissolution of metals by plotting anodic and cathodic polarisation curves. The electrochemical data show that small additions of noble metals to titanium bring about passivity and a marked decrease in the rate of corrosion

are reducing, and it is because palladium has a low hydrogen over-voltage and a high exchange current for the hydrogen-ion reduction process that it is effective in such solutions. The surface of the palladium-titanium alloy forms a bi-electrode or galvanic couple with a mixed potential in the passive potential region, whereas the potential of pure titanium falls in the active potential region.

In addition to palladium, tests were carried out on titanium alloyed with small amounts of the other platinum metals, rhenium, gold, silver and copper. As expected the effectiveness of the various additions is in roughly the same order as their hydrogen overvoltages—platinum, palladium, rhodium, iridium and ruthenium produce the best results, osmium and rhenium are intermediate in effect, gold is beneficial only at higher concentrations and silver and copper, with high overvoltages, are detrimental.

Experiments have shown that whereas titanium is completely dissolved in boiling hydrochloric and sulphuric acid solutions saturated with oxygen, the corrosion rate of the palladium-titanium alloy is only 0.005 inch per year. The effect of platinum and palladium additions to titanium on corrosion rate in boiling hydrochloric acid is shown in the graph. In both solutions the maximum benefit is obtained with as little as 0.1 per cent palladium. In addition to their overwhelming superiority in reducing solutions, palladium-titanium alloys also have the advantage that they become passive in aggressive solutions with concentrations of oxidising agent insufficient to passivate unalloyed titanium.

The addition of these small quantities of palladium has no effect on the mechanical properties of titanium—the palladium-containing alloy can be hot- and cold-worked without difficulty. It is estimated that the addition of 0.1 per cent palladium will add about 28 cents per pound to the price of titanium, which does not seem excessive in view of the benefits gained.