

Increasing the Acid Resistance of Stainless Steels

INFLUENCE OF ADDITIONS OF PLATINUM METALS

Recent Russian work by Tomashov and his colleagues (1-6) has demonstrated the possibility of considerably assisting the passivation of 18-8 type stainless steels in aqueous sulphuric acid by the addition of small amounts of noble metals, especially platinum and palladium.

The modern theory of passivation, developed particularly in Germany by Bonhoeffer, Franck and their colleagues, and independently studied in the USSR, is the starting-point of the work. When any metal is made the anode in an acid solution it first dissolves to a soluble product at an increasing rate, equivalent to the current density, as the anode potential is made more positive. However, at a certain limiting potential and limiting current density, the production of sparingly soluble oxides becomes thermodynamically possible, and kinetically easier than the formation of the soluble product—partly, indeed, because the limit of its solubility has been reached in the layer of acid solution adjacent to the anode. The new product is formed as a compact layer on the anode surface, and provided that the anode potential remains more positive than the limiting value, the metal is protected from all but the smallest attack, being termed “passive” or “passivated”.

Chemical passivation of a metal, without the necessity of an external cathode to send current to the anodic zones, is readily achieved if the acid solution contains a cathode reactant that can react rapidly by cathodic reduction on the metal itself, so producing the necessary rise of potential and high current density at the anodic zones. For pure iron, the strong oxidising agent nitric acid is such a reactant, and if sufficiently concentrated can, as is well

known, produce complete passivation. Chromium, and stainless steels containing it, are much more easily passivated; not only is a much less positive anode potential required to produce chromium oxide, but the rather stable oxide film originally on the metal may greatly assist by much restricting the anodic zones required to be passivated, so that the current available from any cathodic zone can operate at a favourably high current density at the anodic zones. Consequently, *mild* oxidising agents present in *low* concentrations, such as dissolved atmospheric oxygen, may often produce passivation of stainless steels in acid solutions, although depassivation at any parts such as crevices that are liable to become starved of oxygen is always a danger.

Titanium requires an even less positive potential for passivation, and the still milder oxidising agent, hydrogen ion itself, can passivate it; consequently titanium readily becomes and remains passivated even in de-aerated acid solutions containing no other oxidising agent than hydrogen ion itself, with evolution of hydrogen gas during the oxide film formation.

Now, if the surface of stainless steels could be made much more catalytically active for the cathodic reduction of oxygen or, still better, of hydrogen ion, larger current densities at more positive potentials could be obtained at any anodic zones. Tomashov and Mdme. Chernova (2) therefore prepared stainless steels containing small additions of noble metals designed to provide especially active cathodic zones for such reactions. Using as a basis a commercial 18 per cent chromium, 9 per cent nickel alloy steel, they added respectively 0.1 per cent platinum, 0.1 per cent palladium, 0.9 per cent palladium and

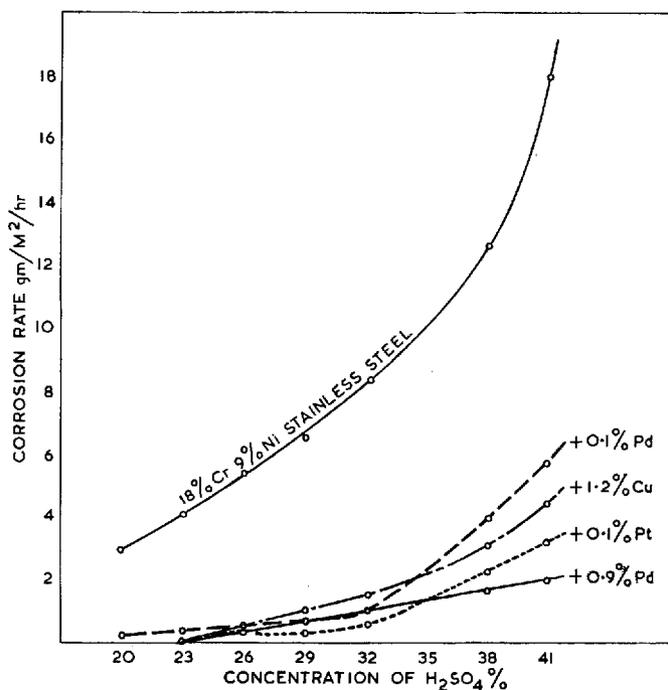


Fig. 1 Rate of corrosion of chromium-nickel stainless steels, alloyed with platinum, palladium and copper, in relation to concentration of sulphuric acid (Tomashov and Chernova)

A basis material of higher chromium content showed a still more marked effect of noble metal additions. Fig. 2 gives the results obtained on adding 0.5 per cent platinum and 0.5 and 1.0 per cent palladium to a straight 27 per cent chromium steel containing no nickel. The region of corrosion resistance to sulphuric acid was here much

1.2 per cent copper. They exposed the four new alloys and the control to aqueous sulphuric acid, in the range 20 to 40 per cent, for 360 hours at 20°C and estimated the corrosion resistance (or completeness of passivation) by the steady rate of hydrogen evolution (after passivation had set in). It may be seen in Fig. 1 that the alloying additions were increasingly effective in the order Cu-Pd-Pt, and that increase of palladium content from 0.1 to 0.9 per cent gave a further useful increase in effectiveness. However, 0.1 per cent of platinum was at least as effective as 0.9 per cent of palladium except at the highest acid concentration.

greater than with the chromium-nickel steel used in the other experiments. Similar results were obtained for a 26 per cent chromium,

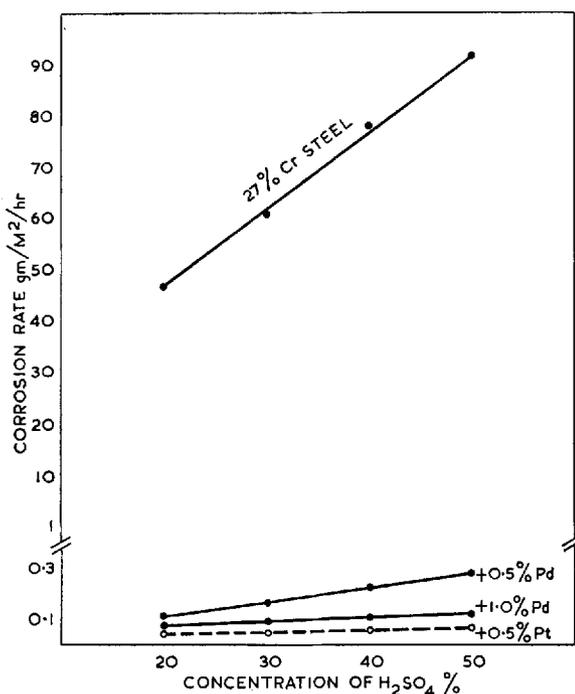


Fig. 2 Rate of corrosion of 27 per cent chromium steel alloyed with platinum and palladium in relation to concentration of sulphuric acid (Tomashov and Chernova)

0.5 per cent nickel steel. The noble metal additions also provided greatly increased resistance of this steel to 10 and 50 per cent formic and 10 per cent oxalic acid solutions maintained at 100°C.

Tomashov and Mdme. Chernova also investigated the effect of additions of noble metal ions to the corrosive acid. For a chromium-nickel stainless steel in 30 per cent sulphuric acid at 20°C, the corrosion rate of 19.9 g/m²/hr without additive was reduced to 0.01 g/m²/hr by the addition of 0.001 g-atom/l. of palladium, copper or silver, and to substantially zero by a similar addition of platinum. They believe that the noble metal deposits in finely divided state on the stainless steel surface, thereby providing active cathodes for the anodic passivation. In the case of the alloyed noble metal additions, these probably dissolve from the surface in the early stages of exposure, along with the less noble basis metals, and then provide active cathodes by re-deposition in exactly the same way.

Although economic considerations will by no means always allow even a 0.1 per cent addition of platinum to stainless steel, it seems likely that for comparatively small components where maximum acid resistance is required such an alloy might well be economically competitive with titanium and other refractory metals and technically at least equal to them. Furthermore, 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.

However, methods of protection based on passivation under conditions near to the border-line between the active and passive states must always be used with caution. The maintenance of the passivating film on chromium-nickel and chromium steels in acid environments depends critically on chromium content, on microstructure and surface condition, on acid concentration and on temperature.

Noble metal additions, by stimulating cathodic reactions, will always raise the anode potential; this is excellent if the rise is sufficient for passivation, but highly deleterious if it is not, because then the rate of active dissolution is markedly increased by the potential rise. With chromium content a little lower, or surface a little rougher, or acid concentration or temperature a little higher, or with a combination of such changes, nearly perfect passivation can give way to very rapid dissolution, and in such cases noble metal additions insufficient to redress the balance would considerably increase the rate of attack.

Consequently, while the Russian work reported here is of the greatest interest, the practicability of noble metal additions must be regarded with some reserve until more extensive trials have been made.

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References

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