Alloying Stainless Steels with the Platinum Metals

INCREASED RESISTANCE TO CORROSION IN ACIDS

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One of the earliest investigators of stainless steels, P. Monnartz (1), reported in 1911 that the rapid corrosion of iron-chromium alloys in certain acids can be suppressed either by winding a platinum wire around the corrosion-test specimen or by adding platinum as an alloying element to the steel. Contact or alloying with platinum changes the electrode potential of the corroding alloy in the positive (noble) direction. A sparingly soluble, protective, hydrated oxide film is formed on the surface of the metal which then becomes "passive". The rate of corrosion is then governed by the solubility of the oxide film in the acid. At those discrete points in the surface at which the film is dissolved, iron and chromium go into solution and react with the environment to form new oxides which repair the break in the passive film. Thus, the passive state is a dynamic, not a static or inert condition, and a continuing, small amount of metal dissolution (corrosion) is required to maintain it.

During the last 25 years Russian investigators, in particular N. D. Tomashov and G. P. Chernova, have studied the effect of alloying additions of platinum and palladium on the dissolution of stainless steels in various acids. Their publications up to 1956 were summarised by T. P. Hoar (2) in this Journal. Additions of 0.1 to 0.5 per cent platinum and 0.1 to 1.0 per cent palladium to iron-18 per cent chromium-9 per cent nickel and to iron-27 per cent chromium stainless steels reduced corrosion of these alloys in 20 to 50 per cent sulphuric acid at 20°C by as much as 99.85 per cent. These noble metal addi-

tions also were found effective in suppressing corrosion in boiling formic and acetic acids. The following is a brief summary of more recent studies on the effect of noble metals in stainless steels.

Since 1956 Tomashov, Chernova and their colleagues have concentrated their attention on the use of palladium additions to various stainless steel compositions in order to reduce corrosion in acids. It was found that an alloy of iron-24 per cent chromium-6 per cent nickel with 0.5 per cent palladium remains passive in 10 per cent sulphuric acid solution up to 100°C (3). Their findings on an alloy of iron-25 per cent chromium-3 per cent molybdenum with 0.5 per cent palladium led to a recommendation of this composition for use in hydrochloric acid solutions up to 1.6 per cent at temperatures up to 100°C. Recently they reported (4) that an iron-40 per cent chromium alloy with 0.2 per cent palladium is resistant to boiling 1 per cent hydrochloric and 40 per cent sulphuric acid at 100°C. The beneficial effects of additions of up to 1 per cent palladium were confirmed by Biefer (5) and by Agarwala and Biefer (6) using an iron-17 per cent chromium stainless steel with and without 2 per cent molybdenum, in converting these alloys to the passive state during exposure to 10 per cent sulphuric acid up to the boiling point.

Earlier this year, Tomashov et al (7) described the effect of palladium additions to austenitic 25 per cent chromium-3 per cent nickel-2 per cent molybdenum-0.8 per cent manganese steels containing up to 1 per cent nitrogen. The alloys were made by plasma

arc melting which makes it possible "to melt steels with nitrogen contents 1.5 to 2 times higher than the standard solubility level of nitrogen in steel of a specific composition at the liquidus temperature". Such nitrogen contents greatly increase the yield strength and make the structure completely austenitic. Additions of 0.2 per cent palladium made this alloy passive in 20 to 30 per cent sulphuric acid in the range of 20 to 100°C and in 1 to 3 per cent hydrochloric acid at 20 to 50°C. No data on the effect of high nitrogen contents or of palladium additions on other forms of corrosion were included.

To observe the accumulation of palladium on the surface of an alloy undergoing self-repassivation, Tomashov et al (8) examined surfaces in the electron microscope after exposure to 10 per cent sulphuric acid at 25°C. Upon immersion in the acid the specimens were activated by cathodic polarisation which initiated dissolution of the alloy. As the 25 per cent chromium alloy dissolved, palladium was concentrated on the surface until the electrode potential changed in the positive (noble) direction and the alloy became passive. On alloys with 0.2 and 0.5 per cent palladium, particles in the range of 200 to 600 Å were found. With increasing exposure time their number, but not their size, increased.

In connection with the development of new ferritic iron-chromium-molybdenum compositions having superior pitting and crevice corrosion resistance, Streicher (9, 10) used all of the platinum metals to produce passivity in boiling 10 per cent sulphuric acid. The effects of these alloying additions on resistance to other forms of corrosion, pitting and crevice attack in oxidising chloride solutions and stress corrosion cracking, were also determined. It was found that a ferritic alloy of iron-28.5 per cent chromium-4.0 per cent molybdenum (later referred to as the 28–4 alloy), which is ductile and weldable, resists pitting and crevice corrosion in 10 per cent ferric chloride solution up to 50°C. And, unlike the austenitic stainless steels, it also resists stress corrosion cracking in various sodium chloride tests, as well as in the severe boiling 45 per cent magnesium chloride test. It has excellent resistance to uniform or general corrosion in organic acids and in oxidising, inorganic acid solutions, but not in inorganic, reducing acids. To produce passivity in boiling 10 per cent sulphuric acid at temperatures up to the boiling point, small amounts of the six platinum metals were added as alloying elements. Some results are given in Table I.

Without noble metals, the rate of attack on the 28–4 alloy is over 52,000 mils per year. Every one of the six platinum metals when present in excess of a certain minimum concentration passivates this alloy. In agreement with previous investigators, acid corrosion is increased by the noble metals when their concentration is below that required to produce passivity. This minimum concentration required to make the alloy passive on immersion in the acid solution decreases with increasing chromium content and varies from 0.005 to 0.02 per cent, depending on the noble metal used. It is independent of the atomic weight, that is, the concentration in atomic per cent.

The determining factors are probably differences in the electrochemical properties of the six platinum metals, electrode potential, hydrogen overvoltage and exchange currents of cathodic reactions taking place on those sites in the surface where the noble metals are exposed to the solution. These electrochemical factors are probably also responsible for the differences, described below, in effects produced by the noble metals on the resistance of the 28–4 alloy to pitting and crevice corrosion. Considerably larger amounts of noble metal (0.5 per cent ruthenium, Table I) additions are required to make the alloy self-repassivating, that is to say, passivity is recovered when the specimen is activated while in the boiling sulphuric acid solution by contact with an iron rod. Passivity and self-repassivation can also be produced in the 28–4 alloy by addition of 2 per cent nickel to

Table I
The Effect of Noble Metal Additions on the Corrosion Resistance of Iron–28.5 per cent Chromium–4.0 per cent Molybdenum Alloy

Noble metal addition Weight per cent		Boiling 10 per cent sulphuric acid		Pitting corrosion (a)		Stress corrosion (b)
		State	Corrosion rate, in mil/year (c)	KMnO$_4$–NaCl	FeCl$_3$	MgCl$_2$
None		active	52,180	R	R	R
Platinum	0.005	active	58,000	R	R	—
	0.006	passive	48	—	R	—
	0.20	passive	1	—	—	R
Palladium	0.01	active	74,000	—	F	—
	0.02	passive	4	—	F	—
	0.20	passive	1	F	F	R
Iridium	0.01	passive	112	R	R	—
	0.10	passive	13	R	R	R
Rhodium	0.005	passive	14	R	F	—
Osmium	0.015	active	76,600	R	R	—
	0.020	passive	26	—	R	—
Ruthenium	0.015	active	62,200	—	—	—
	0.017	active	—	—	—	—
	0.02	passive	60	R	R	R
	0.20	passive	9	—	R	R
	0.30	passive	2	R	R	R
	0.50	passive*	3	—	R	cracked in 17 h (d)

*self-repassivating   R–Resistant; F–Fails
(a) 2 per cent KMnO$_4$-2 per cent NaCl at 90°C, simple immersion. 10 per cent ferric chloride, FeCl$_3$. 6H$_2$O, at 50°C with crevices.
(b) Boiling (155°C) 45 per cent MgCl$_2$, U-bend specimen. R–no cracking after 2400 h exposure.
(c) Thousandths of an inch per year.
d) No cracking in 26 per cent NaCl at 200°C.

this composition with the same effect on other forms of corrosion attack as that of the 0.5 per cent ruthenium addition.

None of the noble metal additions to the 28–4 alloy affected its excellent resistance to stress corrosion cracking in the severe, boiling 45 per cent magnesium chloride test, except the large addition of 0.5 per cent ruthenium. However, when this 0.5 per cent ruthenium alloy is tested in various sodium chloride environments up to 200°C, there is no cracking observed (11).

Because the sodium chloride tests are much more like actual service environments, they are of greater significance as a guide for practical applications of these alloys than the tests in boiling 45 per cent magnesium chloride.

Without noble metal additions the 28–4 alloy resists pitting and crevice corrosion both

Table II
Comparison of Pitting Resistance in Halide Media

Alloy	Permanganate-chloride at 90°C (a)	Ferric chloride at 50°C (b)	Bromine-bromide at room temp. (c)	Sodium hypochlorite at room temp. (d)
AISI 316	F	F	F	F
Carpenter 20 Cb–3	F	F	F	F
Hastelloy C	R	R	F	F
Titanium	R	R	R	R
Fe–35%Cr	F	F	F	F
Fe–28%Cr–4%Mo	R	R	R	R
Fe–28%Cr–4%Mo+Pd	F	F	F	—
Fe–28%Cr–4%Mo+Rh	R	F	F	—
Fe–28%Cr–4%Mo+Pt	R	R	F	—
Fe–28%Cr–4%Mo+Ir	R	R	R	—
Fe–28%Cr–4%Mo+Os	R	R	R	—
Fe–28%Cr–4%Mo+Ru	R	R	R	R

R—Resistant; F—Fails.

(a) 2 per cent $KMnO_4$–2 per cent NaCl. (b) 10 per cent $FeCl_3.6H_2O$, with crevices.

c) 54.5 per cent Br_2+20.6 per cent $ZnBr_2$. (d) 0.1 per cent NaClO with Teflon® crevices.

in the potassium permanganate-sodium chloride solution at 90°C and in the 10 per cent ferric chloride solution at 50°C. Well-known alloys, such as Type 316 stainless steel (iron-18 per cent chromium-9 per cent nickel-2.5 per cent molybdenum) and Carpenter 20 Cb-3 (iron-20 per cent chromium-35 per cent nickel-2.5 per cent molybdenum-3.0 per cent copper), are severely corroded in these two oxidising chloride tests, Table II. Only the nickel-base Hastelloy alloy C (nickel-16 per cent chromium-16 per cent molybdenum) and titanium are resistant. Additions of iridium, osmium and ruthenium are without effect on the pitting and crevice corrosion resistance of the 28-4 alloy in the above two pitting tests. However, even the smallest amounts of palladium, to date the most frequently used of the noble metals to produce passivity, destroy the excellent resistance to pitting of

the 28-4 alloy, Tables I and II. Rhodium does not impair resistance in the potassium permanganate-sodium chloride test, but destroys it in the more severe ferric chloride test.

Some of the alloys were tested in two even more aggressive solutions, bromine in zinc bromide and sodium hypochlorite, Table II. Note that among the materials tested for comparison, only titanium is resistant in all solutions. Platinum additions to the 28-4 alloy cause it to fail in the bromine-bromide solution. Thus, of the six platinum metals only iridium, osmium and ruthenium can be used to produce passivity of stainless steels in sulphuric acid without impairing resistance to pitting and crevice corrosion in oxidising chloride and bromide environments. Of these, ruthenium, because of its lower cost, appears to be the preferred metal for producing resistance to acid corrosion in stainless steels.

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Temperature Measurement and Control

THE ADVANTAGES OF METAL-SHEATHED PLATINUM THERMOCOUPLES

The urgent need to conserve natural resources requires that the most careful appraisal be made of the many uses to which these resources are put; in particular by the industrialised countries of the world. The recent realisation that supplies of fossil fuels are not inexhaustible has prompted the investigation of many manufacturing processes where fuel savings might be achieved, and one outcome has been a better understanding of the contribution that accurate temperature measurement and control could make to both industrial efficiency and energy conservation.

At the Tempcon '77 conference held recently at Wembley, Middlesex, papers were presented covering many aspects of the control and measurement of both low and high temperatures, either directly or by remote control. In one of these papers, by P. I. Roberts of Johnson Matthey Metals, the characteristics, development and uses of platinum metal mineral insulated thermocouples were described.

Such thermocouples, insulated with refractory but sheathed in a metal—usually a platinum group metal—have a number of important advantages compared with conventional thermocouples which are both insulated and sheathed with refractory materials. These benefits include flexibility, smaller diameter, lower thermal mass so quicker response time, and superior resistance to mechanical and thermal shock.

Metal-clad thermocouples tend to be thermo-electrically less stable than refractory sheathed ones when used at temperatures above 1200°C, and this is caused by the transfer of rhodium to the negative limb, mainly from the metal sheath but also from the positive limb. Such effects can be greatly reduced in a number of ways which were described by the author.

First the quality of the insulation is a very important factor because, when sintered, it is capable of restricting the transfer of rhodium oxide in the vapour phase. Alternatively for use at higher temperatures the air in the metal sheath can be removed and replaced with an inert gas such as argon which is then sealed into the unit. For applications at particular temperatures it is possible to select platinum alloys for the thermocouple limbs so that rhodium loss has negligible effect on the electromotive force generated. By using such techniques the advantages of these thermocouples are gained and the problem of thermo-electric drift avoided.

One particularly interesting application of metal-sheathed platinum thermocouples featured in the paper was in the French nuclear industry. It was reported that no changes were detected in the thermo-electric output of platinum : 13 per cent rhodium-platinum thermocouples, enclosed in a composite sheath of 5 per cent rhodium-platinum and stainless steel, following irridation experiments lasting 150 days. This was most interesting as prior to the quoted work it had been considered that neutron bombardment would cause rhodium to transmute to palladium, resulting in calibration drift. Work on this subject is continuing and further papers are expected shortly.