

Platinum Metals in Stainless Steels

PART II: FURTHER CORROSION AND MECHANICAL PROPERTIES

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The first part of this paper reviewed the effects of sulphuric acid on stainless steels modified by platinum metals additions, much of the original work having been carried out by Russian researchers. Now corrosion in other media, and oxidation, are considered and a review of the limited data that are available on mechanical properties is presented. It is concluded that, in particular circumstances, improved material properties can be obtained by the addition of platinum group metals to iron-base alloys.

Corrosion in Halide Solutions

The chloride ion is probably the greatest source of damage to stainless steels, causing rapid degradation of passive films, leading to pitting, crevice corrosion and possibly stress corrosion cracking of loaded components. The effect of noble metal additions on the stress corrosion cracking performance of steels is reviewed later; the results of work involving hydrochloric acid, ferric chloride, sodium hypochlorite, potassium permanganate-sodium chloride and bromine solutions are now considered.

The alloys described by Streicher (18), Bieffer (19) and Agarwala and Bieffer (20) and referred to in the previous section, were also evaluated in pitting and/or crevice corrosion tests in chloride media. Bieffer tested alloys in 1N HCl and 1N FeCl₃ solution at room temperature, with weight loss over four hours immersion being reported; Streicher assessed his alloys in terms of pitting or crevice corrosion. A representative selection of results are shown in Tables VI, VII and VIII, respectively.

It is apparent that palladium additions to AISI 430 (or variants), Table VII, increase the weight loss in chloride environments, the severity of attack increasing with increasing palladium content. With regard to the Fe-28Cr-4Mo alloy, Table VI, noble metal additions below a critical level exacerbate corrosion in boiling 10 per cent sulphuric acid, but above the critical value they deeply passivate the steel. Pitting resistance, however, is frequently impaired and only ruthenium, iridium and osmium can be added with impunity. Lower molybdenum levels rendered the ruthenium-modified steels susceptible to pitting, while the addition of 0.1 per cent nickel to the 0.01 per cent ruthenium steel (which is active in boiling 10 per cent sulphuric acid) rendered it passive, retaining its pitting resistance. The addition of 0.2 per cent silver did not passivate the steel, while 0.2 per cent gold passivated the steel with immunity to crevice corrosion in ferric chloride but failed by pitting in potassium permanganate/sodium chloride solution.

Russian workers have, in general, tested various alloys in hydrochloric acid and reported corrosion rates and electrochemical parameters. They suggest that while palladium additions may increase the tendency of steels to pitting, such additions also broaden the range of acid concentration and temperature over which the steels are passive (21). Outside this range, however, the palladium steels are found to have enhanced corrosion rates, see Tables IX (16) and X (22) and Figures 11 and 12 (22).

It is apparent that the pitting potential is reduced with palladium additions, while the corrosion potential is increased. The rapid dissolution characteristics are obvious for the low palladium steels while the increased

Table VI										
Effect of Noble Metal Additions on the Corrosion of Fe-28Cr-4Mo (18)										
Alloy composition, weight per cent					10% H ₂ SO ₄ at 100°C		Pitting corrosion**			
Fe	Cr	Mo	Ni	Noble metal	State	Corrosion, 10 ⁻³ inch/yr	A	B	C	D
Balance	28	4	—	None	AC*	52,180	R*	R	R	R
Balance	28	4	—	0.005 Pt	AC	58,000	R	R	F*	—
Balance	28	4	—	0.006 Pt	P*	48	—	R	F	—
Balance	28	4	—	0.01 Pd	AC	74,000	—	F	F	—
Balance	28	4	—	0.02 Pd	P	4	—	F	F	—
Balance	28.5	4.5	—	0.015 Ru	AC	62,200	—	—	R	R
Balance	28.5	4.0	—	0.02 Ru	P	60	R	R	R	R
Balance	28.5	4.0	0.1	0.01 Ru	P	41	R	R	R	R
Balance	28.5	4.2	—	0.005 Rh	P	14	R	F	F	—
Balance	28	4	—	0.01 Ir	P	112	R	R	R	—
Balance	28.5	4	—	0.01 Os	AC	57,800	—	—	R	—
Balance	28.5	4.2	—	0.015 Os	AC	76,600	R	R	R	—
Balance	28.5	4	—	0.02 Os	P	26	—	R	R	—

* AC = active, P = passive, R = no pitting, F = crevice corrosion

** Test conditions: A = 2% KMnO₄ + 2% NaCl at 90°C, B = 10% FeCl₃·6H₂O at 50°C, C = 54.5% Br₂ + 20.6% ZnBr₂, D = 0.1% NaClO with crevices

passivation range for the 0.5 per cent palladium steel is also apparent, with rapid depassivation occurring above 0.45N HCl. The passivity of the 0.5 per cent palladium steel in 0.3N HCl is apparently maintained up to 100°C. At this temperature the time to passivate palladium modified oKh₂₅M₃T steel was noted, Table XI (22). Clearly, increased palladium additions decrease the time to passivation, a fact reflected

in various corrosion rate diagrams. Despite the reduction in pitting potential with increased palladium additions, however, no steel exhibited pits, due presumably, to insufficient potential shift during corrosion.

Potential shifts of steels Kh₂₅ and Kh₂₅M₂ with or without palladium in 3 per cent hydrochloric acid at various temperatures were plotted by Chernova (15).

Table VII							
Corrosion Behaviour of AISI 430 Alloy Variants in Various Media (19)							
Steel number	Alloying addition, per cent	Weight losses in 4-hour tests at room temperature, mg/cm ²					
		1N H ₂ SO ₄		1N HCl		1N FeCl ₃	
9A	None	11.8	11.8	6.7	4.9	13.1	10.9
9B	0.06 Pd	14.2	13.4	8.4	6.4	39.6	41.5
10C	0.1 Pd	40.7	37.6	32.0	24.0	38.0	41.7
10D	0.26 Pd	134	105	194	151	39.0	42.1
3B	0.46 Pd	0.4	0.7	59.9	40.7	43.8	44.6
4C	0.99 Pd	0.1	0.7	144	104	42.6	41.2
4D	1.91 Pd	0.2	0.3	193	147	44.1	47.9

Table VIII
Corrosion Behaviour of AISI Type 430 Stainless Steel in Various
Aerated Solutions at 240°C (20)

Steel number	Alloying elements, per cent	Weight losses after 4 hours at 24°C, mg/cm ²			
		1N H ₂ SO ₄	1N H ₂ SO ₄ + 0.5N NaCl	1N HCl	1N FeCl ₃
J-3-2	2.1 Mo	5.5	1.9	1.2	4.8
J-4-2	2.05 Mo, 1.15 Pd	0	2.4	51	21.1
J-7-2	1.84V	8.9	2.8	2.5	8.0
J-8-2	1.89V, 1.06 Pd	0.02	6.0	77	16.0
J-11-2	2.06W	6.3	3.2	2.5	6.0
J-12-2	2.0W, 1.06 Pd	0.04	22.0	101	21.4
A	None	12.8	4.7	7.4	5.8
4C	0.99 Pd	0.4	72	124	41.9
H-1	3.09 Mo	2.3	1.2	0.6	—
H-2	3.07 Mo, 0.19 Pd	0.5	5.4	6.7	—
H-3	3.03 Mo, 0.48 Pd	0	1.3	26.6	—
H-4	3.09 Mo, 0.96 Pd	0	1.9	44.4	—

Table IX
Corrosion Rates of Various Steels in Hydrochloric Acid Solutions
at 20°C and 50°C (16)

Alloy type	Corrosion rate, g/m ² .h			
	HCl solutions at 20°C			HCl solution at 50°C
	1%	2%	3%	1%
Cr-Mn-Ni-Mo	0.012	0.1	1.42	0.13
Cr-Mn-Ni-Mo + 0.2 Pd	0	0.26	0.18	0.11
Cr-Mn	41.4	70.3	97.0	163.9
Cr-Mn + 0.2 Pd	4.4	212.3	282.3	15.4
Cr-Mn-Ni	4.6	8.06	10.22	24.8
Cr-Mn-Ni + 0.2 Pd	0.035	4.8	36.9	0.35
Cr-Mn-Mo*	13.0	16.3	17.9	90.9
Cr-Mn-Mo + 0.2 Pd*	0.073	2.0	12.9	0.38
Cr-Mn-Mo + 0.2 Pd**	0.036	1.6	7.0	0.68
Cr-Mn-Mo**	5.6	12.5	12.0	64.4

Table X
Corrosion Potentials (E_{corr}) and Pitting Potentials (E_{pit}) of 0Kh25M3T and
Palladium Modified Variants in 0.3N HCl against Normal Hydrogen Electrode (22)

Steel	25°C		50°C	
	E _{corr}	E _{pit}	E _{corr}	E _{pit}
0Kh25M3T	+0.40	+1.14	+0.24	+0.53
0Kh25M3T + 0.1Pd	+0.27	+0.96	+0.24	+0.4
0Kh25M3T + 0.2 Pd	+0.24	+0.47	+0.26	+0.35
0Kh25M3T + 0.5 Pd	+0.3	+0.46	+0.26	+0.37

* Alloy numbered 18

** Alloy numbered 27

Both the simple chromium steel (Kh25) and the molybdenum-containing steel were active at all temperatures, while palladium additions bestowed various degrees of passivity upon them. The molybdenum steel, however, generally passivated more rapidly, probably due to molybdenum accumulation. The cathodic process is more efficient on molybdenum than on the base alloy, but not as efficient as on palladium. Due to the concentration differences, however, molybdenum rapidly accumulates and hinders the effect of palladium. This is indicated by monitoring the currents on the steels while maintaining their potential in a cathodic regime, as shown in Table XII on page 148.

Corrosion in Other Media

The performance of the chromium steel Kh27 with palladium additions in formic and oxalic acids at 100°C was investigated by Tomashov (11), Table XIII, and shows similarity with its behaviour in sulphuric solutions, that is, rapid dissolution of the base alloy with the addition of palladium resulting in passivity, the percentage addition required to passivate increasing with the severity of the environment.

Platinum (0.5 per cent) was added to AISI 304 stainless steel by Greiss (23) and exposed to flowing uranyl sulphate or copper nitrate solutions at 250°C. At low flow rates the surface regression was reduced from 0.035 inch/year to 0.015 inch/year through this addition. At high flow rates the difference was minimal, and though even in rapidly flowing uranyl sulphate/copper nitrate/heavy water the corrosion of the same steels was reduced from 0.3 to 0.014 inch/year.

Stress Corrosion Cracking

In 1979 the effect of elementary additions on the stress corrosion cracking of austenitic stainless steels was reviewed by Hänninen (24). The general findings indicate a detrimental effect of noble metal additions to such steels.

These results were confirmed by Chaudron, who showed a progressive reduction in the life

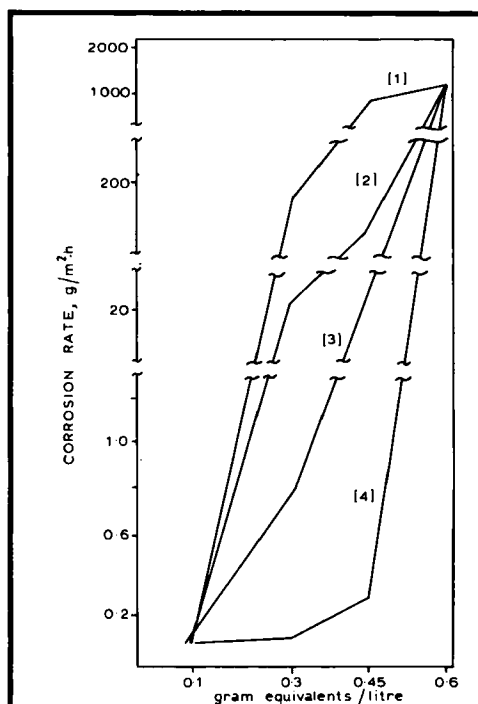


Fig. 11 The influence of the hydrochloric acid concentration on the corrosion rate of: [1] 0Kh25M3T, [2] 0Kh25M3T + 0.1%Pd, [3] 0Kh25M3T + 0.2%Pd, [4] 0Kh25M3T + 0.5%Pd at 100°C; from Tomashov, Chernova and Markova (22)

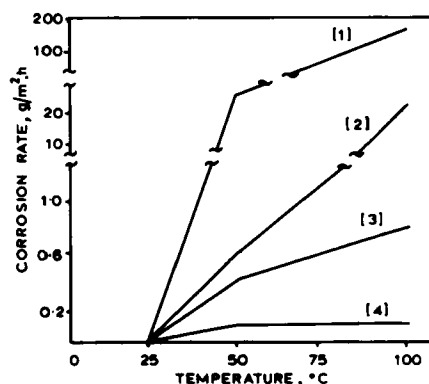


Fig. 12 The influence of temperature on the corrosion rate of: [1] 0Kh25M3T, [2] 0Kh25M3T + 0.1%Pd, [3] 0Kh25M3T + 0.2%Pd, [4] 0Kh25M3T + 0.5%Pd in 0.3N hydrochloric acid; from Tomashov, Chernova and Markova (22)

Palladium addition, per cent	0.3N HCl	0.45N HCl	0.6N HCl
0	Only passive 25°C	—	—
0.1	1 hour	2–3 hours	no passivation
0.2	5 minutes	1 hour	no passivation
0.5	< 1 minute	1 minute	no passivation

of 18Cr-10Ni stainless steel in boiling magnesium chloride with increasing platinum additions (25).

Streicher, however, tested Fe-28Cr-4Mo containing 0.5 per cent ruthenium in sodium chloride solutions at temperatures up to 200°C and found no loss of resistance due to the noble metal addition, lives of up to 1440 hours being achieved without cracking (18). The sodium chloride test, it is claimed, is a better guide to service performance than the more often used magnesium chloride test, in which the same alloy failed in less than 15 hours. The failure of this material was found to be due to transgranular cracking. Van Rooyen suggests that the addition of platinum tends to induce this failure in industrial purity steels (26), although in very pure austenitics the tendency is to intergranular cracking, especially in high nickel steels.

Many authors, however, report noble metal-containing alloys generally show a marked tendency to intergranular failure (27, 28, 29), the latter reference indicating the initial stages of fracture of AISI 446 + 1 per cent platinum to be transgranular with later predominance of intergranular failure.

The stress corrosion performance of Fe-15Ni-20Cr with 1.5 per cent additions of palladium, rhodium, iridium, ruthenium and gold, in boiling magnesium chloride (154°C) was investigated by Staehle (27). Results of this work clearly show the detrimental effect of

these additions. Although the base alloy failed by transgranular cracking, the mode of failure of noble metal containing alloys was predominantly intergranular, and as no precipitates could be seen at grain boundaries when examined by scanning electron microscopy this effect could not be attributed to selective corrosion. This failure mode was also observed for noble metal containing samples tested in MgCl₂ + NaOH, the hydroxide being added to reduce the hydrogen ion concentration (and hence limiting the $H^+ + e^- \rightarrow \frac{1}{2}H_2$ reaction).

Staehle continued to make electrochemical studies of corroding/cracking wire samples. The open circuit potentials of the alloys during stressed exposure to magnesium chloride at

Steel designation	Corrosion current, i_{corr} , mA/cm ²
Kh25	18.8
Kh25M2	40.8
Kh25M2Pd	57.9
Kh25Pd	99.1

Table XIII				
Effect of Cathodic Additives, Platinum and Palladium, on the Corrosion Rate of Kh27 Steel in Formic and Oxalic Acids at 100°C (11)				
Cathodic additive	Test duration, h	Corrosion rate, g/m ² .h		
		10% Formic acid	50% Formic acid	10% Oxalic acid
Without additives	1	343	498	38.3
	10	Complete dissolution	Complete dissolution	7.8
0.1% Pt	1	0.6	75	2.3
	10	0.15	8.6	0.32
0.5% Pt	1	2.2	0.4	1.0
	10	0.11	0.05	0.12
0.7% Pd	1	1.4	3.1	1.1
	10	0.09	0.6	0.25
1.1% Pd	1	4.5	0.7	1.0
	10	0.33	0.08	0.1

154°C were recorded for the alloys containing noble metals. Just before fracture the potentials of the samples were found to rise rapidly and to peak immediately before failure. As previously noted in sulphuric acid the noble metal additions were found to accelerate the reduction kinetics in magnesium chloride. This correlates well with tests carried out in MgCl₂ + NaOH solutions in that on removal of the cathodic species (H⁺) the noble metal-containing alloys became more resistant to failure. Nielsen suggests this behaviour to be due to hydrogen entry and permeation kinetics (29). Hence as platinum increases the hydrogen exchange current (*i*₀), the extra hydrogen evolved would enter the stressed austenitic lattice and increase the tendency to cracking. The disposition to intergranular cracking may be explained by the increased passivity of the bulk material restricting dissolution except at the grain boundaries, where there would be relatively little noble metal.

Nielsen backed up his theories on hydrogen

permeation by testing AISI 446 containing 1 per cent platinum in lithium chloride with thiourea at 170°C (the latter promoting hydrogen entry). The base alloy was totally resistant without thiourea but failed in 20 and 89 hours with thiourea added. The platinum-modified alloy had increased susceptibility in both media. Fracture surfaces were akin to those produced by cathodic charging with hydrogen.

High purity 18Cr-8Ni steels with 0.1 per cent platinum addition were investigated by Montuelle (28) who again observed a drastic reduction in life, from 1000 hours to 50 hours, when exposed to boiling magnesium chloride at 154°C under a load of 33 hectobars. Similarly, a 1 per cent platinum addition to 18Cr-14Ni alloy reduces virtually to zero the critical stress at which the alloy is susceptible to stress corrosion.

It has generally been assumed that the cold worked structure is related to the stress corrosion phenomenon in that a planar dislocation

structure leads to susceptibility, while the cellular structure is thought to be resistant. The addition of platinum, however, to the 18Cr-14Ni steel (which on working generates a cellular dislocation network, and is resistant to stress corrosion) makes the steel very susceptible to cracking, although it retains the cellular structure which is thought to be immune. Additions to steels which are already susceptible, and which have planar dislocation structures, increases the susceptibility but induces a change to cellular morphology.

Hydrogen Embrittlement

The Russians, Levchenko (30) and Arkharov (31), have studied a particular form of hydrogen embrittlement, referred to as "flaking", in steels designated 34KhN3M and 40KhN to which various levels of palladium had been added. "Flaking" is a form of hairline cracking, the "flakes" appearing as bright, round or oval spots on fracture surfaces.

Samples of various diameters were charged with hydrogen at 1100°C for 5 hours, left at room temperature for 10 days, and then annealed at 650°C. The samples were then fractured and the flake density determined. In the work by Levchenko three hydride-forming additives, palladium, cerium and zirconium, were added at 0.3 per cent. The flake density was plotted against sample diameter and cross sectional area for both air cooled and quenched samples. Clearly, palladium additions reduce the susceptibility of the steel to this failure, the reduction in sensitivity being related to palladium content (31), Figure 13.

The beneficial effect of palladium was proposed as being due to the modification of hydrogen traps within the steel, rather than to palladium-hydrogen bonding. When hydrogen is absorbed it either remains active (mobile) or is trapped at boundaries, for example between ferrite and carbide. It is the active hydrogen that results in "flaking". If the traps are modified so that increased amounts of hydrogen can be held, the flake sensitivity will be reduced. This theory was tested by Arkharov, who determined the rate of

hydrogen evolution from charged steels as the temperature increased, at 20°C/min (31), Figure 14(a). It would be expected that the resultant curve would rise to a maximum as the diffusion rate of hydrogen increases with temperature, then fall as the steel becomes exhausted. The actual curves, however, show two maxima, indicating entrapment. Similarly, samples were held at room temperature for long periods and the total evolution of hydrogen from the sample during that time determined, Figure 14(b). The difference between that amount and the equilibrium solubility of hydrogen in steel gives a measure of the internal adsorption of hydrogen (δ), hence:

$$\delta = \frac{C^{\circ}_H - V}{C^{\circ}_H} \times 100$$

where C°_H = equilibrium solubility of hydrogen in steel at 1100°C ($\text{cm}^3/100\text{g}$) which is approximately 6.0 cm^3 per 100g; V = volume of hydrogen evolved from steel at room temperature over 200 hours ($\text{cm}^3/100\text{g}$).

Plotting δ as a function of the palladium content shows clearly the increasing entrapment of hydrogen in palladium steels, Figure 15.

Oxidation

Little information on the oxidation of stainless steels containing platinum group metals is available, although Chaudron (25) tested an experimental 18Cr-12Ni alloy containing 3 per cent platinum in superheated steam at 500°C and 710 psi for 1000 hours, and

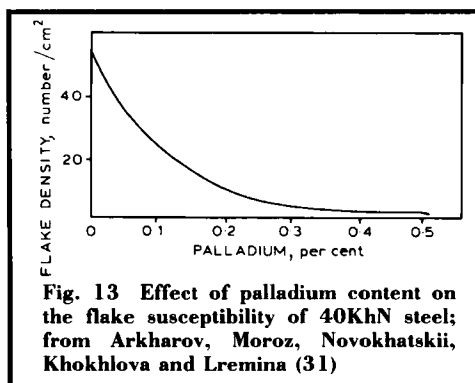


Fig. 13 Effect of palladium content on the flake susceptibility of 40KhN steel; from Arkharov, Moroz, Novokhatskii, Khokhlova and Lremina (31)

discovered a much reduced weight gain over the platinum-free alloy (9 mg/dm² against 111 mg/dm²). Similarly, a 1 per cent platinum addition was found to improve the oxidation of an 18Cr-10Ni steel by approximately 20 per cent (in steam at 600°C, at 995 psi for 6 days), while a 0.1 per cent addition had no effect.

With a view to improving strength without loss of oxidation resistance, Saller investigated platinum and palladium additions of up to 20 per cent in Fe-25Cr-5Al alloys (32). Both metals had a beneficial effect on stress rupture strength, but below 5 per cent little effect on oxidation resistance at 1200°C was observed. Above this, platinum increased the weight gain of the alloy substantially, while palladium continued to have only minor effects.

Mechanical Properties

No systematic investigation of the effects of noble metals on the mechanical properties of stainless steels appears to have been done, though several workers have determined the

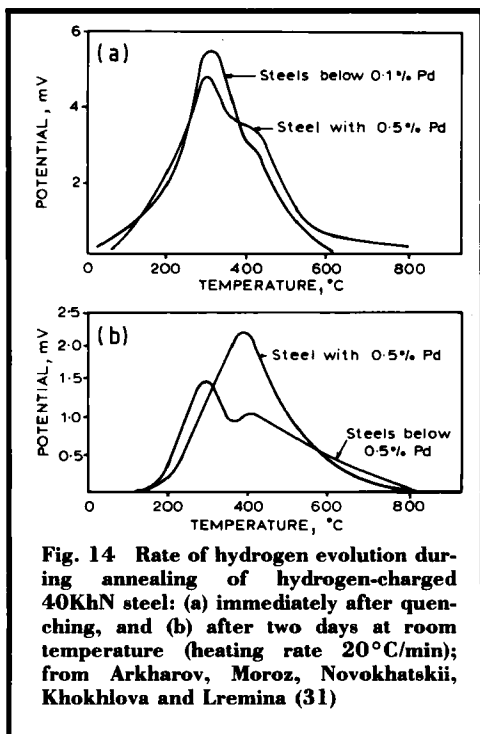


Fig. 14 Rate of hydrogen evolution during annealing of hydrogen-charged 40KhN steel: (a) immediately after quenching, and (b) after two days at room temperature (heating rate 20°C/min); from Arkharov, Moroz, Novokhatskii, Khokhlova and Lremina (31)

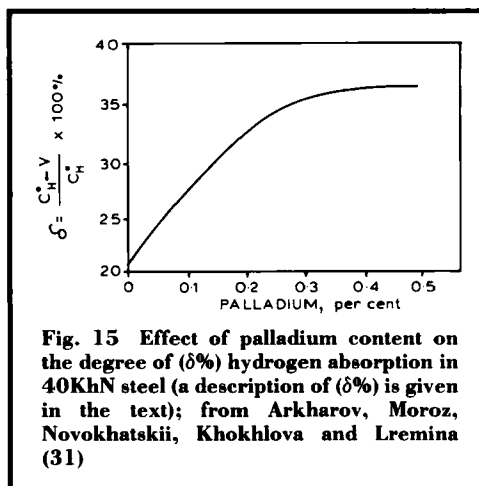


Fig. 15 Effect of palladium content on the degree of (δ%) hydrogen absorption in 40KhN steel (a description of (δ%) is given in the text); from Arkharov, Moroz, Novokhatskii, Khokhlova and Lremina (31)

mechanical properties of experimental alloys, in order to assess required loading for subsequent stress corrosion testing.

The effect of various "tertiary" additions, including platinum/palladium and gold, on the mechanical properties of transformable Fe-Mo-C alloys has been studied by Irani and Honeycombe (33).

The Fe-4Mo-0.2C alloy undergoes a martensitic transformation when it is water quenched from 1250°C; a further quench in liquid nitrogen ensures the transformation is complete. Additions of several elements including palladium and gold were made to high purity melts of these alloys at trace levels, that is 0.06 atomic per cent (0.45 wt per cent gold, 0.058 wt per cent palladium). The alloys were tempered for up to 1000 hours at temperatures between 500 and 700°C, and the change in hardness over this period was monitored.

At various stages, samples were examined by transmission electron microscopy in order to correlate structural effects with the age hardening behaviour. The base alloy is martensitic after the stated heat treatment, and after tempering in the range 200 to 500°C, yields a Widmānstätten iron carbide (Fe₃C) precipitate. Molybdenum carbide (Mo₂C) displaces iron carbide as the dominant precipitate in steels tempered above 500°C, appearing as needles on the {100} ferrite planes only after peak

hardness. The structural changes that occur up to peak hardness are described below:

550°C, 65 hours; 660°C, 1 hour: Molybdenum rich zones align in cube directions. Zones are disc shaped, 10 to 20 nm diameter and a few atoms thick. The diffraction pattern did not reveal any identifiable compound (precipitate) in these zones but did indicate molybdenum enrichment.

550°C, 200 hours: Zones found to be larger, 30 to 60 nm diameter, and more numerous.

Beyond Peak Hardness: Mo_2C needles precipitate, later replaced by M_6C -type carbides. Recrystallisation of the ferrite lamellae to equiaxed structure completes the process.

The addition of the trace elements generally increases peak hardness, and reduces the tempering time required to achieve peak hardness. Carbide-forming additions including niobium, chromium, titanium, and tantalum, allow the retention of alloy hardness, while the strength of an alloy containing non-carbide forming additions, such as palladium and gold, falls rapidly on over-ageing.

The addition of gold, coupled with tempering at 500°C, gives rise to the highest overall hardness; palladium is less effective although still inducing enhanced hardness over that of the base alloy. Structurally, the tempering process in alloys containing trace additions follows the same course as that of the base alloy, for example zone formation and Mo_2C precipitation. Just after peak hardness, however, the gold-containing alloy showed fine gold particles between the molybdenum-rich zones, coarsening with increasing tempering temperature.

Low carbon steels (0.01 per cent) with gold additions were tested with a view to eliminating carbide effects. A degree of hardening could be seen in the base alloy but the addition of 0.03 atomic per cent gold was still effective. It is suggested by the authors that the influence of the trace additions is on zone formation. Since precipitates are not seen until after peak hardness, it is apparent that it is the zones that are responsible for the hardening effect. It is possible that the size of the gold atom causes strain in the steel matrix and encourages easy zone

formation. This cannot be a complete explanation, however, as smaller atoms also show a hardening effect. It is interesting to note that of all the additions, only gold is seen to cluster during tempering, while the tempering resistance of steels with carbide-forming additions is attributed to the formation of a fine dispersion of coarsening resistant alloy carbides.

On a different note, Demo reports the effect of precious metals in changing the ductility of welds in high chromium ferritic steels (34). As the chromium content of such steels increases, the resulting weldments become increasingly brittle; however this can be alleviated by adding platinum, palladium, silver, aluminium or copper to the weld.

Concluding Remarks

The addition of noble metals to steels has a distinct but variable effect upon their corrosion resistance and mechanical properties; the magnitude of this effect depends upon the noble metal addition, the composition and structure of the steel and the environment to which the steel is subjected.

It is apparent that low levels of noble metal additions can have marked effects on the properties of iron-base alloys. In particular, the corrosion performance of these alloys in non-oxidising media is considerably modified, by virtue of the unique properties of platinum group metals in reducing hydrogen over-voltage. The ease of the hydrogen reaction $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$ on a noble metal surface would force the potential of the corroding steel to achieve values otherwise unobtainable, except by impressed polarisation. The effect of this can be to take the alloy into a regime of passivity, whereby the formation of insoluble surface films occurs and metal dissolution (corrosion) is reduced to minimal levels. It is equally possible, however, that the induced potential shift suffices only to enhance the corrosion rate. It is significant to note that noble metal additions have, if anything, detrimental effects on the corrosion resistance of steels in oxidising media, such as nitric acid. The observed

accumulation of noble metals as particulates on corroding surfaces explains many of the phenomena observed in this type of alloy:

(i) A critical noble metal level must be exceeded in order to achieve passivity, otherwise enhanced corrosion occurs. If insufficient noble metal is available on the surface the potential shift induced will serve only to increase the corrosion current, and hence, the corrosion rate.

(ii) Noble metal-modified steels initially corrode rapidly, before becoming passive. It is obvious that the initial surface concentration of noble metal is very low, and that it is necessary to dissolve a certain volume of material to allow a significant accumulation of the noble element on the surface prior to passivation.

(iii) The improvement in corrosion resistance achieved with noble metal additions is less for higher alloyed steels, for example molybdenum-containing steels, than for simple alloys. If the alloy constituent accumulates at the surface faster than the noble element (as it will invariably do, due to the relative concentrations) the effect of the noble metal will be restricted due to its limited surface area.

(iv) Surface passivation is achieved more rapidly, and more effectively, when the noble metal constituent is finely distributed over the passivating surface. Clearly, an increase in the microcathodic surface area by an increase in the surface-to-volume ratio of noble metal particles would be consistent with an increase in the efficiency of the reduction process, that is hydrogen reduction, and consequently an aid to more effective passivation.

The marked effect of the noble metal additions on the cathodic process ($H^+ + e^- \rightarrow \frac{1}{2}H_2$) is apparent, while the effect on the anodic process is more obscure and undoubtedly less dramatic. The most noticeable effect is a general shift in the pitting potential of steels containing platinum, palladium, rhodium and, to a small extent, gold.

Susceptibility to hydrogen embrittlement can be reduced by the addition of a noble metal such as palladium. In this case it is claimed that palladium modifies sites within the steel at which hydrogen may be trapped, so reducing

the amount of "active" hydrogen available to cause embrittlement.

The improved cathodic efficiency of steels containing noble metals is, however, not always beneficial, and indeed has been deemed responsible for a reduction in resistance to stress corrosion cracking. The enhanced evolution of hydrogen is claimed to lead to increased entry of hydrogen into the steel structure which, under severe testing conditions such as boiling magnesium chloride, gives rise to premature failure. In less stringent, and possibly more realistic tests, however, no loss of resistance is noted. Platinum additions were found to have distinct morphological effects and caused modification of the cold worked dislocation structures, and also altered the failure mode from transgranular to intergranular cracking. There is sufficient evidence to suggest that, although some marginal improvement in the general corrosion resistance of austenitic steels results from the addition of noble metals, an increase in sensitivity to stress corrosion cracking may be expected, and to a degree which makes this class of steel an unlikely proposition for noble metal alloy modification.

It is clear, therefore, that noble metals are capable of causing distinct physical/mechanical changes in steels. The addition of gold to a transforming steel has shown that a remarkable degree of strengthening can be achieved by controlling heat treatment procedures, and this strengthening has been associated with short range ordering of gold within the steel matrix. Noble metal additions to welds in ferritic steels have had beneficial effects on weld ductility, a traditional problem in these steels.

Another benefit that can result from noble metal additions is improved oxidation rates for steels at high temperatures. Similar effects have been noted elsewhere for nickel-base alloys containing platinum group metals.

The concept of adding noble metals to iron-base alloys has technical and practical credibility. Platinum, palladium, rhodium, iridium, osmium and ruthenium, have been thoroughly investigated in this context, particularly the elements platinum and palladium.

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Cathodic Modification with Platinum Metals

The use of the platinum group metals to modify the cathodic reaction on stainless steels, chromium-based alloys and titanium-based alloys has been under investigation for some considerable time. From the available research data which has been reviewed recently (A. Higginson, "Passivation of Cathodically Modified Alloys", *Br. Corros. J.*, 1989, **24**, (4), 297-302) platinum and the other five platinum group metals would seem to be obvious choices for improving the high temperature passivation characteristics of these materials when subjected to non-oxidising acidic media. What has limited the application of the results of these investigations is the level of noble metal addition required to achieve the benefits observed, and which consequently limits commercial viability. As pointed out by Higginson, even at 0.2 weight per cent, this addition can constitute the major cost of the cathodically modified alloy.

The benefit of achieving rapid and sustained passivity in chromium-, titanium- and iron-based alloys by the use of the platinum group metals does, however, warrant re-examination; in particular a study of the synergistic effects between the platinum group metals and elements such as molybdenum and nickel should be pursued. Higginson points out these areas for further investigation, and in addition highlights the generally poor performance of cathodically modified alloys in chloride-containing environments.

Finally, with respect to platinum group metal modified austenitic stainless steels in chloride-

containing environments, it is worth mentioning the work of H. E. Hänninen, *Int. Met. Rev.*, 1979, (3), and G. Chaudron, U.S./Euratom Programme, Project No. 293, Eurac Reports 1749 and 1804. Findings from their research would indicate that although some marginal improvement in the general corrosion resistance of austenitic steels can be achieved by the addition of noble metals, an increase in the sensitivity to stress corrosion cracking may be expected, and to a degree which could make this class of material an unlikely proposition for noble metal alloy modification.

I.R.M.

A Stimulating Electrode

An electrical prosthesis may be used to artificially restore some function of the body which has been lost due to accident or disease. A review of the role of the platinum metals in this important biomedical application has been published here previously (P. E. K. Donaldson, *Platinum Metals Rev.*, 1987, **31**, (1), 2-7).

Now a paper from the University of Michigan describes a process for producing passive multi-electrode stimulating probes for use in neutral prostheses, based on a planar iridium oxide film (S. J. Tanghe, K. Najafi and K. D. Wise, *Sens. Actuators B*, 1990, **B1**, 464-467). Activated iridium oxide stimulating sites are shown to be capable of delivering very high charge densities to the tissue on a chronic basis.