

Platinum Metals In Stainless Steels

A REVIEW OF CORROSION AND MECHANICAL PROPERTIES

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The range of iron-based materials known as stainless steels are used throughout the world to manufacture products requiring special resistance to corrosive environments. The corrosion resistance of these materials depends largely upon the chromium content, which is usually between 10 and 30 per cent of the alloy constitution. Of equal significance is the ability to vary the structure of the alloy between ferritic, austenitic and martensitic, by control of the type and level of additional elements. There are, however, many corrosion limiting factors which restrict the use of each type of steel, and the addition of noble metals to the iron-base constitution, to improve this situation, has been considered. This article summarises most of the published work on the effects of platinum group metals on the corrosion and mechanical properties of stainless steels, but excludes investigations of non-stainless steels.

Two previous reviews of the effects of adding platinum group metals to iron-based alloys have been published in this Journal previously (1, 2). Information from these sources has been assessed and, where appropriate, included here for the sake of completeness.

Alloy Compositions

Major element compositions of the steels reviewed here are generally self-evident, especially those under the Soviet Designation system described later. The compositions of some of the steels referred to in the text are not

obvious, however, and these are given below, in the Appendix.

Alloy Designations

Much of the work featured in this review was originally published in the Russian language, and Soviet alloy designations used in this review have been transliterated from the Russian rather than translated, in order to avoid confusion with Western alloys which are similar, but not identical. The explanation of these designations is based on information contained in the "Handbook of Soviet Alloy

Appendix								
Composition of Various AISI Steels								
Steel designation	Composition, per cent							Reference
	Fe	Cr	Si (max.)	Mn (max.)	C (max.)	Other	Noble metal	
AISI 304	Balance	18.0–20.0	1.0	2.0	0.08	8–12.0 Ni	Pt	23*
AISI 430	Balance	14.0–18.0	1.0	1.0	0.12	—	Pd	19,20
AISI 446	Balance	23.0–27.0	1.0	1.5	0.20	0.25N	Pt	29*

*References numbered 21 to 35 will appear in Part II of this paper

Compositions" (3) and a British Iron and Steel Industry publication (4), while a complete description of steel and alloy compositions is given in a Soviet standard (5).

In Soviet alloy steel designations, the following symbols represent the following elements:

A Nitrogen	G Manganese
N Nickel	T Titanium
B Niobium	K Cobalt
P Phosphorus	Ts Zirconium
D Copper	Kh Chromium
R Boron	V Tungsten
F Vanadium	M Molybdenum
S Silicon	Ya Aluminium

When the percentage of the element is not greater than about 1 per cent the letter for the element is not followed by a number. If the amount of the element is greater than 1 per cent, a number representing the content is placed to the right of the symbol, for example 4 per cent nickel is represented by N₄.

The average carbon content is shown to the left of the letters, as hundredths of one per cent. In the case of a very low carbon content (less than 0.08 per cent), the numeral "0" is placed before the letters. The letter A appended to these designations denotes narrower composition limits, and low sulphur and phosphorus contents, and must not be confused with the symbol A representing nitrogen. Frequently, the letter L is used as a suffix to denote a cast steel.

Several groups of steel designations carry a prefixed letter which indicates a particular purpose or characteristic, such as, A- free machining, E- magnetic, Zh- straight chromium stainless, R- high-speed, Sh- ball-bearing, E- electrical and Ya- chrome-nickel stainless. The numbers following these letters are not normally indicative of the actual composition.

Platinum Metals-Modified Steels in Sulphuric Acid Solutions

Many of the investigations carried out on platinum group metals-modified steels have been done under the auspices of two notable Russian scientists, N. D. Tomashov and G. P. Chernova. Much of the work consisted of

simple gravimetric analysis, but some important electrochemical studies of the corrosion behaviour of platinum group metals-modified steels were also made.

Hoar (1) quotes early work by Tomashov and his colleagues (6-12) on the beneficial effects of additions of platinum and palladium to a commercial 18 per cent chromium-9 per cent nickel steel when subjected to various concentrations of sulphuric acid at room temperature. Similar effects have been recorded by Tomashov and Chernova for Kh₂₇, 0Kh₂₅T, Kh₂₈TL, Kh₂₅, Kh₂₅M₂ and a plasma melted Cr-Ni-Mn-Mo steel. A summary of these results is given in Figure 1.

In the same way Tomashov, Chernova and Volkov (13) noted that a 24Cr-6Ni steel became passive with the addition of 0.5 per cent palladium when exposed to 10 per cent sulphuric acid at temperatures up to 100°C, while a 0.2 per cent palladium addition to Fe-40Cr alloy confers resistance to 40 per cent sulphuric acid at 100°C (14). The steel Kh₂₅ with and without 0.7 per cent palladium was tested in 30 per cent sulphuric acid by Tomashov and Chernova (10) and its corrosion monitored by the evolution of hydrogen. At the same time the potential of the sample was recorded, Figure 2.

From these results it was shown that the initial corrosion rate increases with the palladium addition, but diminishes rapidly after a critical period. The sample potential showed corresponding behaviour. The mechanism proposed was that on initial immersion in a non-oxidising medium the corrosion reaction, that is the anodic reaction $M \rightarrow M^+ + e^-$, is sustained by the cathodic reaction $H^+ + e^- \rightarrow \frac{1}{2}H_2$, the rate of which is determined by the hydrogen over-potential at the surface of the test piece. For surfaces with a high hydrogen over-potential, that is surfaces which are slow to discharge hydrogen, the rate of the cathodic reaction (hydrogen evolution) will govern the corrosion reaction (metal dissolution), the result being steady state dissolution of the material.

With noble metal-containing alloys, however,

Fig. 1(a) Corrosion of Kh27 chromium steel, alloyed with cathodic additions, in sulphuric acid at room temperature:

- [1] Kh27,
 - [2] Kh27 + 0.41%Cu,
 - [3] Kh27 + 2.67%Cu,
 - [4] Kh27 + 0.71%Pd,
 - [5] Kh27 + 0.5%Pt,
 - [6] Kh27 + 3.0%Pt;
- from Tomashov and Chernova (10)

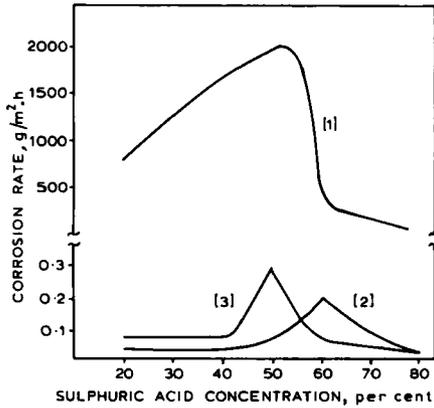
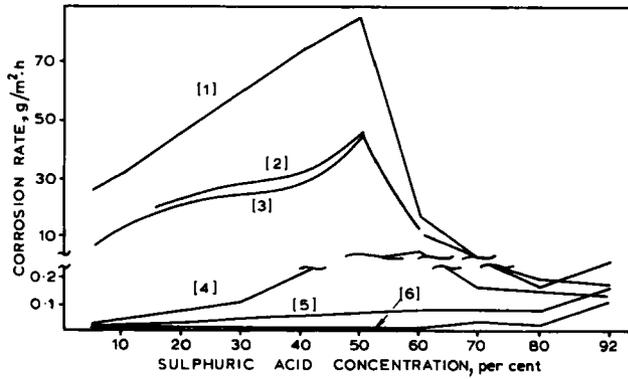


Fig. 1(b) (left) Corrosion of Kh27 chromium steel in sulphuric acid solutions at 50°C: [1] Kh27, [2] Kh27 + 3%Pt, [3] Kh27 + 3%Pd; from Tomashov and Chernova (10)

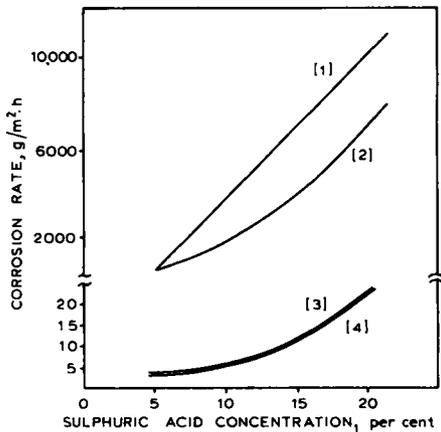


Fig. 1(c) Effect of palladium on the corrosion rate of 0Kh25T and Kh28TL in sulphuric acid at 100°C. Test time = 5 hours: [1] 0Kh25T, [2] Kh28TL, [3] 0Kh25T + 0.5%Pd, [4] Kh28TL + 0.5%Pd; from Tomashov, Chernova and Kupriyanova (35)

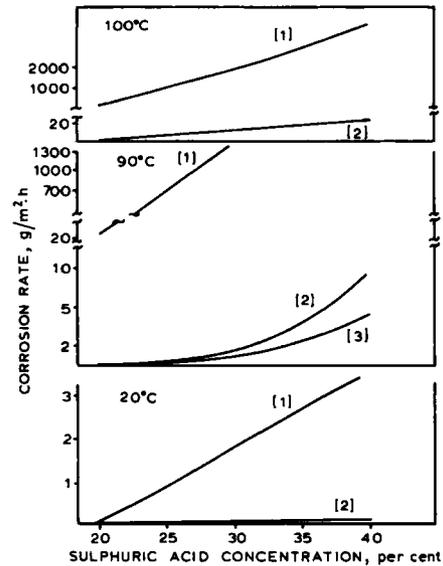


Fig. 1(d) Mean corrosion rate of a plasma melted FeCrNiMo steel in sulphuric acid: [1] Base alloy, [2] Base + 0.2%Pd, pre-activated, [3] Base + 0.2%Pd, non-activated; from Tomashov, Lakomskii, Chernova, Torkhov, Chigirinskaya and Slyshankova (16)

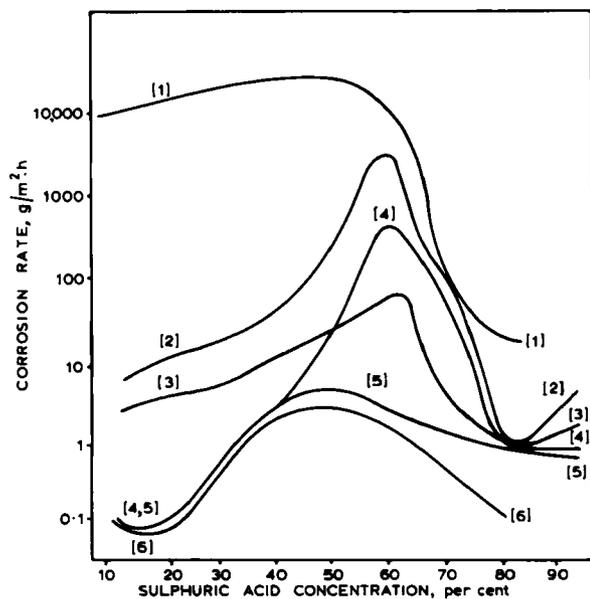


Fig. 1(e) Corrosion of Kh27 chromium steel, alloyed with cathodic additions, in sulphuric acid at 100°C:

- [1] Kh27,
 - [2] Kh27 + 0.7%Pd,
 - [3] Kh27 + 1.1%Pd,
 - [4] Kh27 + 3%Pd,
 - [5] Kh27 + 0.5%Pt,
 - [6] Kh27 + 3%Pt;
- from Tomashov and Chernova (10)

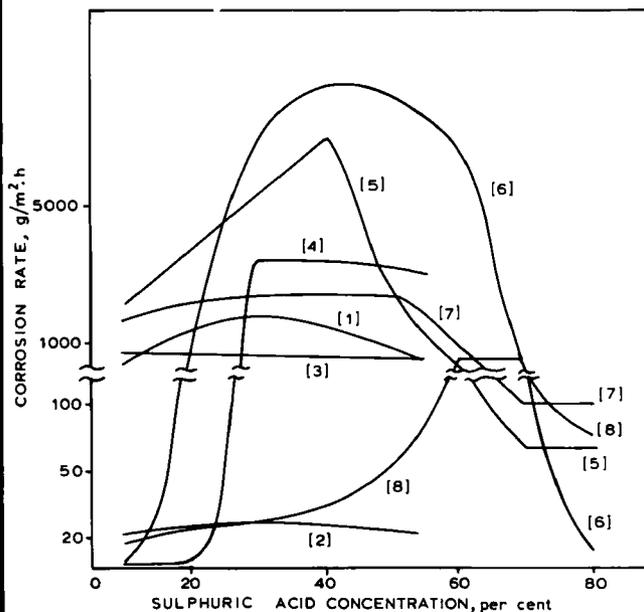


Fig. 1(f) Mean corrosion rates of steels:

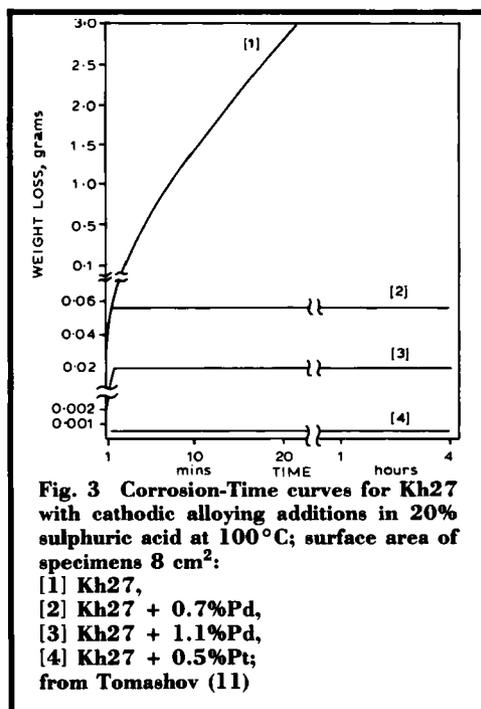
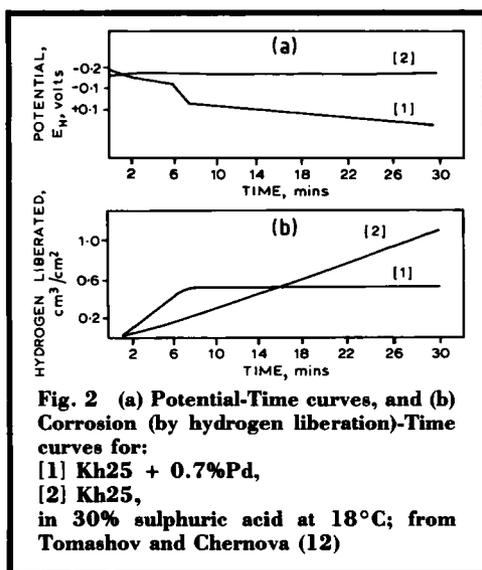
- [1] Kh25,
 - [2] Kh25 + 0.3%Pd,
 - [3] Kh25M2,
 - [4] Kh25M2 + 0.3%Pd,
- all at 80°C; and
- [5] Kh25,
 - [6] Kh25 + 0.3%Pd,
 - [7] Kh25M2,
 - [8] Kh25M2 + 0.3%Pd,
- all at 100°C in sulphuric acid solutions. Test times: steels containing palladium, 5 hours; steels without palladium, 30 minutes; from Tomashov, Golovanenko, Ul'yanin, Chernova and Goronkova (15)

the hydrogen over-potential of the original surface is reduced and enhanced corrosion occurs. As dissolution of the less stable components occurs, the noble metal accumulates as discrete particles on the surface where the hydrogen over-potential is very low, and hydrogen evolution occurs at these sites. As the over-potential

is low, the equilibrium $H^+ + e^- \rightarrow \frac{1}{2}H_2$ is shifted far to the right, and the corresponding potential shift is sufficient to take the sample into a passive regime with an accompanying reduction in the corrosion rate. The effect of rapid corrosion followed by passivation is consistently seen in non-oxidising acid media, as

shown in Figure 3, and Tomashov claims that the majority of the weight loss observed from Kh25 and Kh24M2 steels containing 0.3 per cent palladium was due to the initial corrosion effect (15). After passivation the maximum weight loss observed was $0.3 \text{ g/m}^2 \cdot \text{h}$ indicating significant passivation.

The variation of sample potential during corrosion can be complex, especially in higher alloy steels. Tomashov plotted the variation of sample potential of Fe25Cr6Ni steel alloyed with 0.1, 0.2 and 0.5 per cent palladium in 10 per cent sulphuric acid at 100°C (13). The corrosion of the base alloy occurred with regular potential variation between -0.26 V and -0.12 V , the corrosion potential of Kh25 steel being determined at -0.26 V . The shift to more noble potentials was thought to be due to the accumulation of nickel on the surface of the steel as corrosion proceeded. Due to the high nickel dissolution rate, however, the potential of the steel did not reach the critical passivation potential, and the steel remained active. The palladium-containing steels, however, show modified potential/time traces. The initial potential arrest at -0.12 V for the 0.1 per cent palladium steel was again thought to be due to nickel accumulation. After dissolution of this



surface, the active corrosion period which followed presumably allowed accumulation of sufficient palladium to maintain the potential at -0.12 V until partial passivation ($+0.01$ to $+0.03 \text{ V}$) took place at a later stage. On higher (0.2 per cent) palladium content steels, palladium accumulates more rapidly, shortening the arrest times and eliminating reactivation periods. The value of the final potential was close to the reversible hydrogen potential on palladium. This undoubtedly is due to the adsorption of hydrogen on the surface accumulation of palladium. The 0.5 per cent palladium addition causes rapid displacement of the potential to a fully passive regime. In this case it is clear that hydrogen evolution cannot be the only cathodic process occurring—the potential is displaced beyond the reversible potential—and oxygen depolarisation must be assumed. It is conceivable that for the lower palladium additions the rate of accumulation of palladium is lower than the rate of hydrogen adsorption. In the case of the 0.5 per cent addition the

Steel	Passivation time, min	Corrosion losses in active period of dissolution, g/m ²	Corrosion losses during test time of 5h, g/m ²	Corrosion rate at corrosion potential (E _H), g/m ²	E _H , volts
OKh25N6T	Not passivated	3800	3800	760	-0.09
OKh25N6T + 0.1Pd	11	358.8	492.8	26.8	+0.042
OKh25N6T + 0.2Pd	2.5	40.4	130.4	18	+0.047
OKh25N6T + 0.5Pd	0.5	26.4	148.9	24.5	+0.055

palladium must accumulate at the surface faster than the hydrogen can adsorb, and the alternative cathodic reaction can be sustained with the associated potential shift.

In a higher acid solution, (20 per cent) no steel passivates fully, although increasing the palladium content reduces the time to partial passivation, even though the final corrosion potentials (and hence corrosion rates) are similar for all the steels tested, Table I.

In hot, 90°C, sulphuric acid solutions of various strengths, Tomashov again followed sample potential during active corrosion (16), Figure 4. The alloy tested was a Fe₂₇Cr₈Ni₂MoMnN steel with 0.2 per cent Pd. In the light of previous comments it would appear that at 20 per cent acid solution a partial passivation occurs due perhaps to the accumulation of molybdenum or manganese on the surface, which would possibly be superseded by passivation due to palladium accumulation. The 40 per cent solution is too severe and no passivation is possible due to a rapid dissolution rate. Between these extremes the sample potential moves rapidly to palladium agglomeration-induced passivation. Results of similar work by Tomashov (15) on very high purity ferritic steels Kh₂₅ and Kh₂₅M₂ (2 per cent molybdenum) with 0.3 per cent palladium additions are shown in Figure 5. Again, the intermediate regime (in this case temperature) results in deeper passivation of the molybdenum bearing steel. Molybdenum, it is

claimed, hinders the passivating effect of palladium (the steel Kh₂₅M₂Pd_{0.3} is only passive up to 50°C). However, it is reported that for passive Mo-Pd steels the corrosion losses are 10 and 20 times less than for similar, simple palladium-containing steels. Molybdenum in palladium-containing steels, when tested in sulphuric acid, reportedly "narrows" the effective acid concentration and temperature band in which the steel will passivate, but also deepens passivation characteristics.

Earlier work by Tomashov compares the performances of three related alloys, containing 3 per cent platinum and 3 per cent palladium

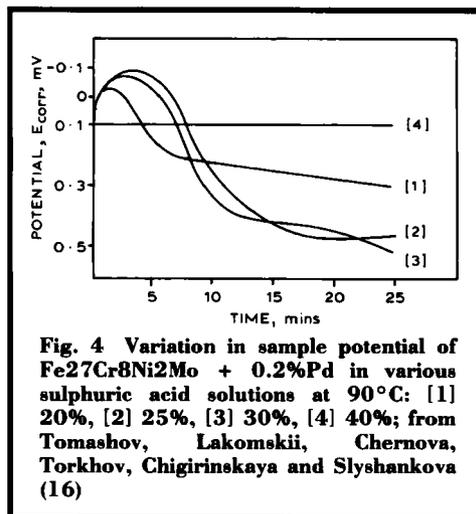
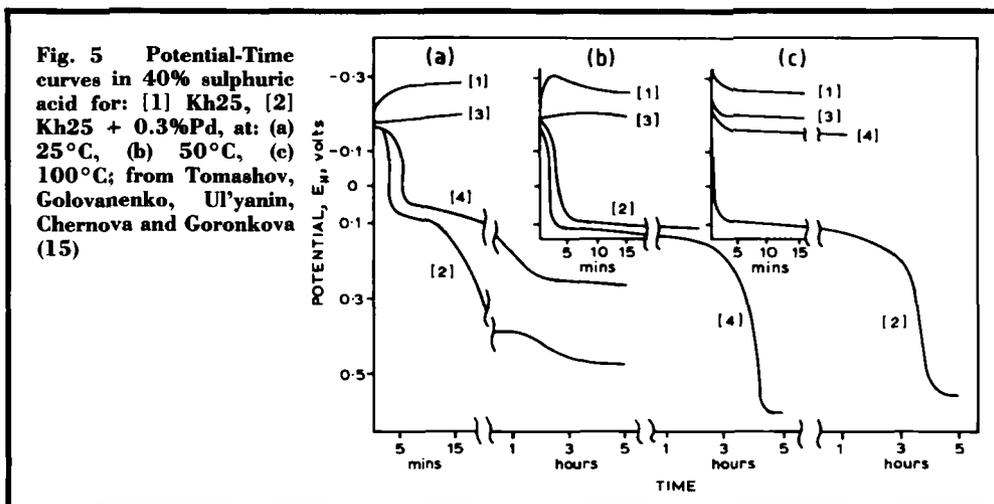


Fig. 4 Variation in sample potential of Fe₂₇Cr₈Ni₂Mo + 0.2%Pd in various sulphuric acid solutions at 90°C: [1] 20%, [2] 25%, [3] 30%, [4] 40%; from Tomashov, Lakomskii, Chernova, Torkhov, Chigirinskaya and Slyshankova (16)



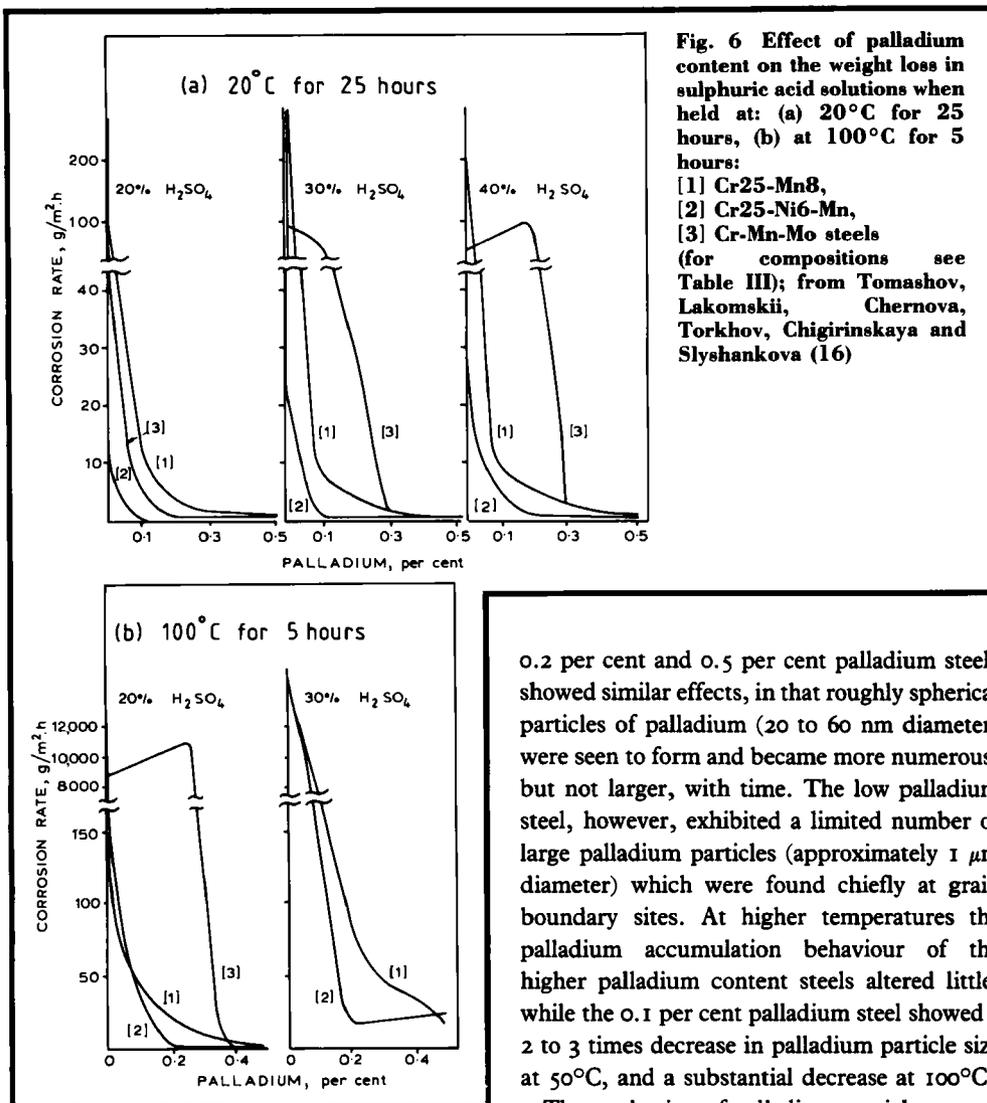
against the base alloy, in 20 per cent and 30 per cent sulphuric at 50°C with respect to their composition and passivation potentials (11), Table II. It is apparent that the corrosion rate of the high nickel alloy is greatly exacerbated by noble metal additions, while that of the intermediate nickel alloy is largely unaltered. The simple chromium alloy, however, is very deeply passivated. The explanation for this effect was that the passivation potential for Kh18N60 is more positive than that for hydrogen ion

depolarisation on palladium/platinum. Consequently, unless an alternative cathodic reaction that would sustain the required potential shift to passivation is available (that is, oxygen reduction), no passivation is possible. However, the enhanced hydrogen reaction rate due to the cathodic additions stimulates the dissolution (corrosion) of the alloy as shown in Figure 5. Similarly, the alloy Kh27 passivates at -0.15 V (S.H.E.), well within the capability of the enhanced hydrogen reaction, while the 9

Table II

Effect of Cathodic Additives Platinum and Palladium on the Corrosion Rate of Chromium and Chromium-Nickel Alloys in Sulphuric Acid Solutions at 50°C (11)

Alloy	Corrosion rate, g/m ² .h		Passivation potential (S.H.E.)
	Sulphuric acid concentration		
	20%	30%	
Kh27	905	1223	-0.15
Kh27 + 3%Pt	0.03	0.015	-
Kh27 + 3%Pd	0.12	0.03	-
Kh18N9	14	25.5	-0.09
Kh18N9 + 3%Pt	7.05	21.0	-
Kh18N9 + 3%Pd	17.9	49.0	-
Kh18N60	1.37	1.97	+0.15
Kh18N60 + 3%Pt	231	254	-
Kh18N60 + 3%Pd	118	190	-



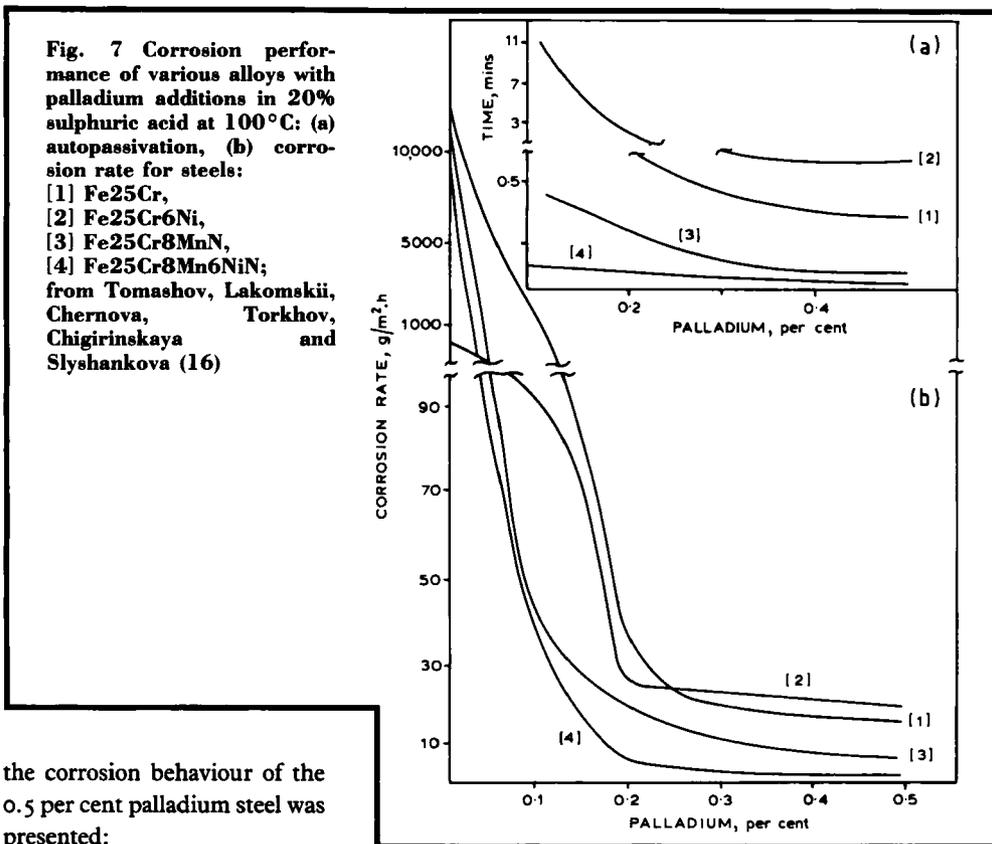
0.2 per cent and 0.5 per cent palladium steels showed similar effects, in that roughly spherical particles of palladium (20 to 60 nm diameter) were seen to form and became more numerous, but not larger, with time. The low palladium steel, however, exhibited a limited number of large palladium particles (approximately 1 μm diameter) which were found chiefly at grain boundary sites. At higher temperatures the palladium accumulation behaviour of the higher palladium content steels altered little, while the 0.1 per cent palladium steel showed a 2 to 3 times decrease in palladium particle size at 50°C, and a substantial decrease at 100°C.

The nucleation of palladium particles occurs at a definite surface supersaturation. Consequently, the higher palladium steels would be expected to nucleate more readily and form more palladium particles of similar size, while at low palladium concentrations the nucleation rate would be somewhat less and the tendency, as was observed, would be to form fewer larger particles. The effect of temperature was to increase the rate of dissolution, increasing the rate of surface enrichment in palladium so allowing more rapid nucleation of particles and hence, a finer particle size.

A simple empirical formula which is based on

per cent nickel alloy only just achieved passivation.

Electron microscopy studies of corroded samples of oKh25T steel with additions of 0.1, 0.2 and 0.5 per cent palladium were undertaken by Tomashov (17). The samples were cathodically activated in 10 per cent sulphuric acid at 25, 50 and 100°C then allowed to corrode without external application of potential. Single and two-stage replicas were taken of the samples after various exposure times, and examined. At room temperature (25°C) both the



the corrosion behaviour of the 0.5 per cent palladium steel was presented:

$$Q = A/n$$

where Q = weight loss in g/cm^2 , n = per cent palladium addition and A = reaction coefficient.

For similar palladium accumulation morphology, the equation is an excellent fit, hence the 0.5 per cent and 0.2 per cent palladium steels follow the stated relationship at all temperatures, as does the 0.1 per cent palladium steel at 100°C . In the low palladium steel, however, as the palladium precipitates coarsen with decreasing temperature so the discrepancy between predicted and actual performance increases, presumably due to the lower palladium surface area presented to support the hydrogen evolution reaction which is necessary to move the steel nearer to passivation.

The effect of varying levels of platinum group metals additions to stainless steels has also been investigated by many other workers, notably

Tomashov (16), Streicher (18), and Biefer (19).

Tomashov extended original work in order to investigate palladium additions up to 0.5 per cent in a range of steels, all of which were plasma melted to increase their nitrogen content to approximately 1 per cent (16). The palladium additions did not affect the microstructure of any of these steels, but hindered activation of the samples (by contact with zinc) for subsequent corrosion testing. Weight loss data in 20, 30 and 40 per cent sulphuric acid at 20 and 100°C are shown in Figure 6, while Figure 7 and Table III show the relationship between corrosion rate, auto-passivation time and palladium content. The higher palladium content steels reduce both the corrosion rate and the auto-passivation time.

The potentials of the alloys in Figure 7 were plotted as corrosion proceeded and showed a rapid rise of potential which corresponded to

Table III															
Times to Reach Autopassivation for Experimental Steels Containing Various Levels of Palladium in Various Sulphuric Acid Solutions (16)															
Conditions of test		Time to autopassivation, seconds													
		Type of steel													
H ₂ SO ₄ , per cent		Alloy designation													
		Cr-Mn					Cr-Mn-Ni				Cr-Mn-Mo				
Temperature, °C	Alloy designation														
	7	8	9	10	11	14	15	16	17	19	20	21	22	23	
	Palladium, per cent														
	0.1	0.2	0.3	0.4	0.5	0.2	0.3	0.4	0.5	0.1	0.2	0.3	0.4	0.5	
20	20	1540	830	168	173	64	154	—	130	108	256	380	150	120	75
	50	218	177	98	36	15	30	18.3	33	36	105	162	54	33	21
	100	21	15	6	4	3	3.6	3.6	5	4	—	—	16.5	4	2.3
30	20	2010	994	272	224	68	200	105	140	117	—	455	337	129	48.5
	100	30	18	5.6	5.3	2.4	7.3	3.8	5.0	4.8	—	—	—	—	—
40	20	2190	1120	327	270	78	258	144	174	160	—	—	—	285	240
	100	—	—	6.8	5.6	3.0	11.8	3.2	7.0	5.5	—	—	—	—	—

Table IV							
Compositions of Experimental AISI 430 Alloy Variants (20)							
Steel number	Base Composition, weight per cent						Alloying Elements, per cent
	C	Cr	Mn	P	S	Si	
J-3-2	0.08	17.36	0.61	0.018	0.021	0.27	2.10Mo
J-4-2	0.08	17.48	0.64	0.020	0.022	0.32	2.05Mo, 1.15Pd
J-7-2	0.07	17.13	0.75	0.006	0.021	0.49	1.84V
J-8-2	0.08	16.96	0.74	0.012	0.022	0.48	1.89V, 1.06Pd
J-11-2	0.09	17.53	0.70	0.021	0.018	0.36	2.06W
J-12-2	0.09	17.49	0.72	0.011	0.018	0.32	2.0W, 1.06Pd
A	0.06	17.38	0.80	0.013	0.018	0.42	—
4C	0.06	16.94	0.76	0.014	0.019	0.44	0.99Pd
H-1	0.05	16.54	0.59	0.017	0.017	0.26	3.09Mo
H-2	0.05	16.24	0.57	0.014	0.016	0.31	3.07Mo, 0.19Pd
H-3	0.05	16.39	0.54	0.017	0.016	0.29	3.03Mo, 0.48Pd
H-4	0.05	16.39	0.50	0.014	0.017	0.32	3.09Mo, 0.96Pd

the initial rapid corrosion rate of the palladium alloys, Figure 8.

Bieffer investigated the performance of the commercial ferritic stainless steel AISI 430 with several element additions (19), one being palladium, in the range 0 to 2 per cent. The effect of the additions was noted primarily on the

anodic and cathodic polarisation curves of the alloys in 1N H₂SO₄ at room temperature.

Palladium has a noticeable effect on cathodic polarisation characteristics. The lower level additions tend to flatten the Tafel portion of the curve, while the higher level additions tend to steepen and displace it, so the intersection

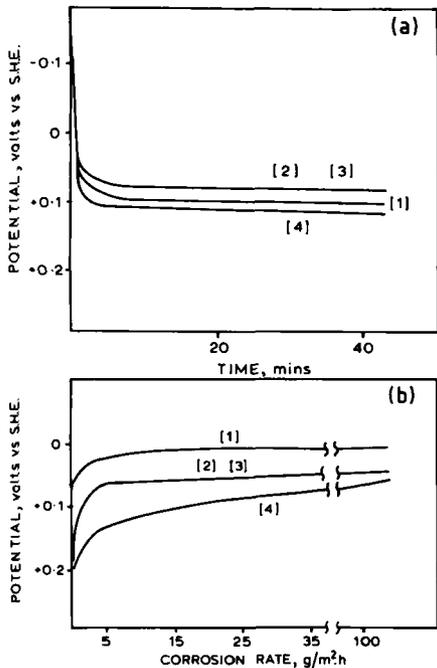


Fig. 8 (a) Variation in sample potential with time of various alloys in 20% sulphuric acid at 100°C for: [1] Fe25Cr, [2] Fe25Cr8MnN, [3] Fe25Cr8Mn6NiN, [4] Fe25Cr6N. (b) Variation in corrosion rate in 20% sulphuric acid at 100°C for: [1] Fe25Cr, [2] Fe25Cr8MnN, [3] Fe25Cr8Mn6NiN, [4] Fe25Cr6N, all with 0.5%Pd; from Tomashov, Lakomskii, Chernova, Torkhov, Chigirinskaya and Slyshankova (16)

of this and the anodic curve—that is, where the electrochemical equilibrium between the two reactions lies—is well into the region of passivity. The subsequent corrosion current, i_{corr} , is therefore reduced to very low levels. The deleterious effect of low level additions, and the highly beneficial effects of higher level palladium additions are clearly shown in Figure 9. By testing in sulphuric acid environments a map of passive/active behaviour of the alloys can be drawn, Figure 10.

Clearly, the addition of 0.99 per cent palladium is effective in inducing passivity at high and low acid concentrations, the base alloy showing rapid dissolution under all conditions.

Fig. 9 Effect of alloying additions on the corrosion performance of AISI 430 in 1N sulphuric acid; from Bieffer (19)

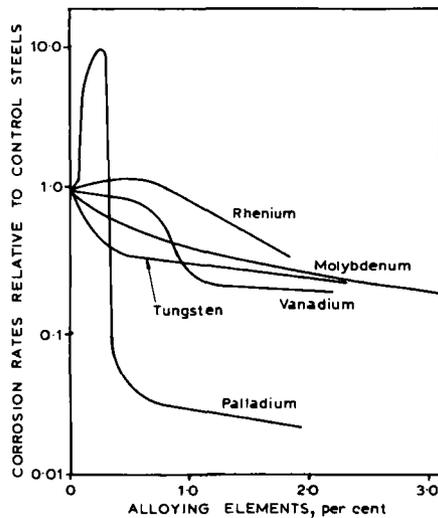


Fig. 10 Active and passive regions for: (a) palladium-containing AISI 430 steel, and (b) unmodified AISI 430 (and AISI 304) in sulphuric acid of various concentrations at the given temperatures; from Bieffer (19)

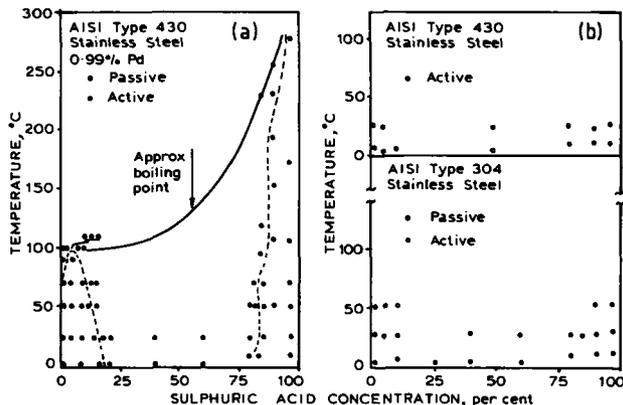


Table V					
Anodic Polarisation Parameters of AISI 430 Alloy Variants from Potentiostatic Measurements in Nitrogenated Solutions at 24°C (20)					
Steel number**	Alloying elements, per cent	In 1N H ₂ SO ₄		In 1N H ₂ SO ₄ + 0.5N NaCl	
		E _{c_{pp}} , mV	i _{c_{pp}} , μA/cm ²	E _{c_{pp}} , mV	i _{c_{pp}} , μA/cm ²
J-3-2	2.10Mo	-412	2,200	-350	5,250
J-4-2	2.05Mo + 1.15Pd	-478	1,300	-385	6,000
J-7-2	1.84V	-435	5,200	—	—
J-8-2	1.89V + 1.06Pd	-500	2,400	—	—
J-11-2	2.06W	-420	5,500	—	—
J-12-2	2.0W + 1.06Pd	-485	2,800	—	—
A	None	-354	34,000	-375	22,000
4C	0.99Pd	-480	6,750	-400	25,000

**See Table IV for steel compositions

Passivity was arbitrarily defined as a positive corrosion potential, and consequently, as passivation can occur at negative potentials, the passive regions are probably much broader. On initial immersion in the acid the potential was found to be negative, changing, in some cases, over 18 hours to a positive potential. This finding is in accordance with the observations of other workers, and corresponds to the formulation of palladium microcathodes on the surface as corrosion proceeds.

Biefer claims that the AISI 430 steel to which 0.99 per cent palladium had been added shows superior performance in concentrated sulphuric acid at high temperatures than the most highly alloyed austenitic steels, although he acknowledges the danger in comparing data from different test procedures (19).

The steels were also similarly evaluated in 1N H₂SO₄ + 0.5N NaCl solution. The base alloy exhibits breakdown of the passive film by pitting in chloride solutions.

Palladium additions cause large increases in the exchange current density (*i*₀) and some decrease in (*i*_{c_{pp}}), where c_{pp} = critical passivation potential, but not enough to cause spontaneous passivation. Biefer goes on to suggest that by modifying the cathodic processes by the addition of palladium and the anodic process by molybdenum addition, for example, substantial improvement in corrosion resistance may be ex-

pected. This theory was investigated in later work by Agarwala and Biefer (20). Alloy compositions are shown in Table IV with polarisation results in Table V.

As in previous work, active/passive maps in temperature/sulphuric acid concentration regimes were plotted for various alloy combinations. The combined addition of palladium and molybdenum passivates the steel over a wider range of dilute acid concentrations than the palladium addition alone, although molybdenum would appear to be detrimental to the resistance of the alloy to corrosion in concentrated acid. The addition of molybdenum does, however, allow the level of palladium to be reduced and still achieve passivity in dilute sulphuric acid. Additions of tungsten and vanadium with palladium have variable effects and seem to be susceptible to low acid concentrations in the range 40 to 70°C. Corrosion resistance in concentrated acid is also inferior to that of a 0.99 per cent palladium alloy.

Results of tests in 1N H₂SO₄ with various percentages of NaCl are given and in general it was noted that with the exception of the 0.19Pd-3.07Mo steel, all the palladium bearing steels spontaneously passivated in 1N H₂SO₄ + 0.5N NaCl, whereas those containing single element additions did not. It is planned to conclude Dr. McGill's paper in the next issue of this journal.

References

- 1 T. P. Hoar, *Platinum Metals Rev.*, 1958, 2, (4), 117
- 2 M. A. Streicher, *Platinum Metals Rev.*, 1977, 21, (2), 51
- 3 "Handbook of Soviet Alloy Compositions", PB 171331, U.S. Dept. of Commerce, OTS Washington D.C.
- 4 "BISI 2000", British Iron and Steel Industry Translation Service Publication
- 5 "Soviet Steel Standards", COST 4543-57 and 4632-51
- 6 N. D. Tomashov, G. P. Sinel'shchikova (Chernova) and M. A. Vedeneeva, *Zh. Fiz. Khim.*, 1949, 23, 3
- 7 N. D. Tomashov and G. P. Chernova, *Dokl. Akad. Nauk SSSR*, 1953, 89, (1), 121
- 8 N. D. Tomashov, *Dokl. Akad. Nauk SSSR*, 1953, 88, (6), 1023
- 9 N. D. Tomashov, G. P. Chernova and R. D. Anashkin, *Trudy Inst. Fiz. Khim. Akad. Nauk SSSR*, No. 5, Issledovan Korrozii Metal. No. 4, 1955, 159-171
- 10 N. D. Tomashov and G. P. Chernova, "Problems of Corrosion and Protection of Metals", *Akad. Nauk SSSR*, 1956, 68
- 11 N. D. Tomashov, "Problems of Corrosion and Protection of Metals", Report of the All-Union Council for the Corrosion and Protection of Metals, *Akad. Nauk SSSR*, 1956, 17
- 12 N. D. Tomashov and G. P. Chernova, in "Passivity and Protection of Metals Against Corrosion", 1967, Plenum Press, New York, Ch. III
- 13 N. D. Tomashov, G. P. Chernova, L. N. Volkov, *Prot. Met.*, 1970, 6, 388
- 14 N. D. Tomashov, G. P. Chernova, L. A. Chigirinskaya and M. F. German, *Werkst. Korros.*, 1976, 27, (9), 636
- 15 N. D. Tomashov, S. A. Golovanenko, E. A. Ul'yanin, G. P. Chernova and A. D. Goronkova, *Zashch. Met.*, 1980, 16, (2), 105
- 16 N. D. Tomashov, V. I. Lakomskii, G. P. Chernova, G. F. Torkhov, L. A. Chigirinskaya and V. A. Slyshankova, *Zashch. Met.*, 1977, 13, (1), 10
- 17 N. D. Tomashov, G. P. Chernova, L. N. Volkov, A. P. Zakharov and Z. E. Sheshenina, *Prot. Met.*, 1973, 9, (3), 289
- 18 M. A. Streicher, *Corrosion*, 1974, 30, (3), 77
- 19 G. J. Biefer, *Can. Metall. Q.*, 1970, 9, (4), 537
- 20 V. S. Agarwala and G. J. Biefer, *Corrosion*, 1972, 28, (2), 64

Rhodium Enhances the Corrosion Resistance of Titanium Surgical Implants

One of the most important properties required of a material to be implanted in the human body is long term biocompatibility; another is resistance to corrosion in the biological environment. A number of physical properties such as good ductility and workability, low density and low elastic modulus are also necessary. Titanium and titanium-6 per cent aluminium-4 per cent vanadium satisfy these requirements, and have been used as surgical implant materials. In mechanically and electrically static conditions, the corrosion rates of these materials in the biological environment are low, but still finite. Thus metal ions are released continuously and may concentrate in the tissues. The long term effects of this are not fully understood but there is some concern, particularly about the effects of aluminium and vanadium present in the alloy.

For this reason efforts are being made to develop new materials with superior properties. Corrosion is essentially a surface phenomenon, so if a material has suitable mechanical properties, it is unnecessary to change the bulk properties by bulk alloying. An improvement may be achievable by increasing the resistance to corrosion of only the surface layer.

Initial results of biocorrosion studies of rhodium and gold implanted into titanium and a titanium alloy, respectively, when tested in non-passivating acid and in passivating saline solutions of the type used to simulate the environment encountered by surgical implant materials, have been published recently (I.-S. Lee, R. A. Buchanan and J. M. Williams, *Mater. Res. Symp. Proc.*, 1989, 110, 687-695). Commercially pure titanium implanted with rhodium showed long term improved corrosion resistance in 1N sulphuric acid solution, as a result of preferential dissolution of titanium and a related build-up of rhodium. The rhodium-enriched surface was also stable in saline solution.

Contaminated Washcoatings

Please note that in the paper entitled "The Effect of Fuel and Oil Additives on Automobile Catalyst Performance" which appeared in *Platinum Metals Rev.*, 1990, 34, (1), 16-24, the two parts of Figure 3 were transposed. As is apparent from the P_2O_5 profiles, the test oils with high phosphorus contents appeared on the left of the page, as a, instead of on the right as b. Any confusion caused is regretted.