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Alloys cathodically modified with noble metals

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The truly remarkable corrosion resistance of alloys containing small amounts of noble metals relies on the principle that the high exchange-current density for the reduction of hydrogen can shift the corrosion potential of the alloy to a value in the passive region, causing it to passivate spontaneously. Research indicates that additions of 0.1 to 0.4% PGMs to chromium in sulphuric acid cause the alloy to self-passivate easily and also increased the corrosion resistance by several orders of magnitude. The effectiveness of the PGMs in promoting corrosion resistance was found to decrease in the order Pt > Pd > Ir > Ru > Os. An enrichment of PGMs at the surface of the alloys occurred during the period of active dissolution. The effect of cathodic additions in ferritic stainless steels became more enhanced with an increase in the chromium content of an alloy. Furthermore, if molybdenum and a PGM occur together in an alloy, a synergistic beneficial effect is exerted on the corrosion resistance. The effect of the cathodic modification of austenitic stainless steels is not as dramatic as for ferritic stainless steels. Little is known about the effect of PGMs on the corrosion behaviour of duplex stainless steels. Work on titanium–palladium alloys led to the development of a commercial titanium–palladium alloy containing 0.2% palladium, which is especially suited to reducing conditions. By contrast with the chromium and stainless-steel alloys, the addition of PGMs to titanium was found not to be detrimental to its corrosion resistance in highly oxidizing media. The surface alloying of materials with PGMs by various methods could prove to be a more cost-effective method than bulk alloying.

1. Introduction

Recently, research on cathodic modifications of alloys with noble metals for the improvement of corrosion resistance has been rather neglected. Only Tomashov's group, Higginson and others at Mintek have apparently been carrying out research in this field. As a result, there has been little discussion of the topic in the literature, and no comprehensive review paper on the subject could be found. The present review, therefore, covers previous work carried out by various groups from different laboratories and, in addition, discusses recent results. Conclusions are drawn from earlier results, and possible areas for future research are outlined. The electrochemical mechanism of cathodic alloying is not covered in the present discussion, since it has been dealt with elsewhere [1].

2. Cathodic modification of chromium and chromium-based alloys

Since 1948, both Tomashov *et al.* and Stern *et al.* have proved that the tendency to passivation and the corrosion resistance of chromium in a non-oxidizing acid environment can be increased by the addition of small amounts of platinum-group metals (PGMs) to these alloys [2–9]. Alloying with these cathodic additives causes dramatic improvements in corrosion resistance, and does not reduce the low-temperature plasticity of the chromium. It therefore opens up extensive possibilities for the use of these alloys in new industrial applications.

2.1. *Effect of the addition of noble metals*

2.1.1. Cathodic modification. Greene *et al.* [5] conducted a comprehensive investigation into the influence of small additions of various PGMs, as well as some other noble metals, on the corrosion resistance of chromium in both non-oxidizing acids (hydrochloric, sulphuric), and an oxidizing acid (nitric). The tests carried out for the determination of the loss in mass in boiling sulphuric acid (5 to 98%), in hydrochloric acid (5 to 15%), and in nitric acid (65%) showed that an addition of as little as 0.1% PGMs to chromium (Cr–0.1% Pt) could cause a decrease in the corrosion rate of the chromium by a factor of 10^5 or more. Whereas each of the alloying additions improved the corrosion resistance in non-oxidizing environments, several of the PGMs, particularly platinum and ruthenium, actually accelerated corrosion in nitric acid, which is a highly oxidizing environment. This phenomenon can be explained by the fact that the corrosion potential of chromium in a boiling solution of 65% nitric acid is very noble, and is very close to the beginning of its transpassive region. Alloying with an inert element having a large exchange-current density for the reduction of nitric acid can shift the existing high positive potential of the alloy into the transpassive region, resulting in an increased dissolution of the

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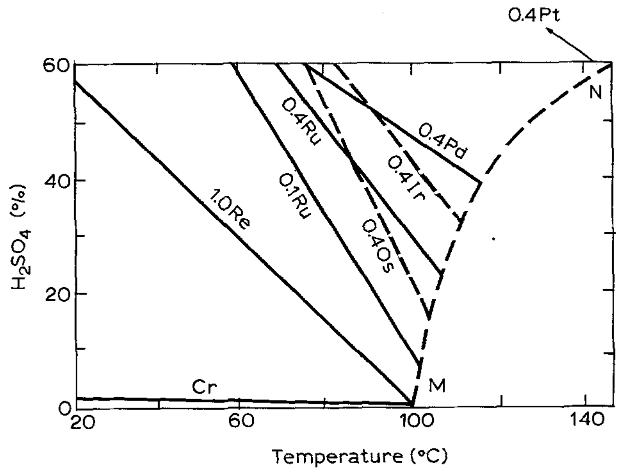

Fig. 1. Effect of the modification of ductile chromium by the addition of rhenium (1%) and Os, Ru, Ir, Pd, and Pt (0.4%) on its passivation and corrosion stability as functions of the concentration and temperature of sulphuric acid.

metal. In electrochemical tests carried out at room temperature, a decrease in the critical anodic current density for passivation was found in all the chromium alloys containing noble elements, except those containing rhenium, silver and gold. The decreasing order of effectiveness of the various alloying additions in causing corrosion resistance in sulphuric and hydrochloric acids is as follows:

$$\mathrm{Ir} > \mathrm{Rh} > \mathrm{Ru} > \mathrm{Pt} > \mathrm{Pd}$$
$$> \mathrm{Os} > \mathrm{Au} > \mathrm{Re} > \mathrm{Cu} > \mathrm{Ag}$$

This can be correlated with the hydrogen-overvoltage behaviour of these elements.

The corrosion of ductile chromium alloyed with ruthenium, osmium, iridium, platinum, palladium, and rhenium in solutions of 5 to 60% sulphuric acid at various temperatures has been described by Tomashov *et al.* in various papers [6–9]. The effect of the different alloying additions on the corrosion stability of ductile chromium in acid at different concentrations and temperatures is summarized in Fig. 1 [10].

Figure 1 depicts the lines separating the regions of the steady, passive, and active states for the different chromium PGM alloys. Below and to the left of the boundary line is the region in which a specific alloy retains a stable passive state, while above and to the right of the boundary line lies the region in which the specific alloy actively dissolves. The lower the concentration of the PGM addition to the alloy, the lower and more to the left shifts the line for the alloy in the graph (e.g. the Cr–0.1% Ru and Cr–0.4% Ru lines on the graph). The dotted curve, MN, represents the boiling points of the sulphuric acid solutions versus their concentrations.

Figure 1 clearly shows that chromium that has no cathodic additives (PGMs) corrodes at a high rate, while cathodically modified alloys self-passivate easily, and their corrosion resistance is several orders of magnitude higher than that of pure chromium. An increase in the concentration of the alloying component also increases the stability of the passive state.

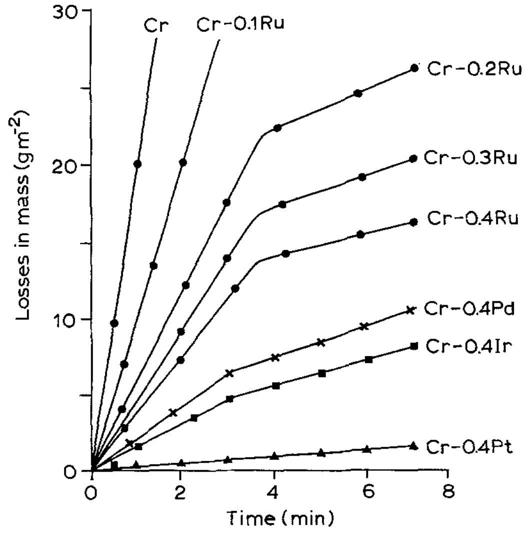

Fig. 2. The dissolution kinetics of plastic chromium and its alloys containing cathodic additions (mass %) in 40% H_2SO_4, 65° C at $E_H = -0.175$ V.

A detailed study of Cr–Pd (0.1 to 0.4%) and Cr–Pt (0.1 to 0.4%), alloys in a 50% solution of sulphuric acid at 98° C [8] revealed that the addition of small amounts of nitrate ions (0.02% NO_3^- or 0.2 g dm^{-3} NO_3^-), which serve as an oxidizing agent, considerably increased the stability of the passive state in this aggressive condition. On the other hand, concentrations of up to 10 mg dm^{-3} of chloride ions in solutions of 40% sulphuric acid at 65° C delayed the onset of self-passivation, and also narrowed the range of the passivation region for ductile Cr–0.3% Ru, and Cr–0.4% Ru alloys [2].

2.1.2. Kinetic effect. Tomashov *et al.* [6, 9, 11, 12] investigated the effect of PGMs on the active dissolution of ductile chromium in sulphuric acid. Results of the dissolution kinetics of ductile chromium alloyed with ruthenium, iridium, palladium, and platinum (0.1 to 0.4%) studied in a solution of 40% sulphuric acid at 65° C and at a fixed potential of − 175 mV/SHE, is schematically depicted in Fig. 2. It is obvious that the PGM alloying elements decrease the anodic dissolution rate of chromium, and also that the corrosion resistance of the alloy depends on the concentration and nature of the alloying addition.

Investigations of the Cr–PGM alloys by electron microscopy after active corrosion had taken place showed that the accumulating PGMs formed separate islets rather than a homogeneous layer on the surface of the alloy. It is presumed that the dissolution of chromium from the Cr–PGM alloy occurs by means of successive transfer into the solution of the atoms that are at the corners and edges of the crystal lattice, and that have an enhanced activity. If these sectors of the crystal lattice are blocked by more corrosion-resistant PGM atoms, anodic dissolution of the chromium atoms that lie on the flat steps of the alloy lattice and that bind more firmly to it will take place less readily. The PGM atoms gradually lose their bonding with the neighbouring chromium atoms, and remain on the surface in the form of adsorbed atoms or adatoms [11–13]. The further surface diffusion of such adatoms results in the formation of microcrystals of pure PGMs, which are metals that preserve the electric contact with the substrate alloy [11, 12]. Thus, with an increase in the PGM content of the alloy, more active surface centres are blocked by the added PGM atoms, and the rate of chromium solution from the alloy in the active state decreases. While Tomashov *et al.* [11–13] do not preclude the possibility of the partial solvation of the PGM atoms, they conclude that the changing distribution of the PGM metal occurs mainly as a result of a surface diffusion mechanism.

The retardation of the anodic dissolution of chromium by all the PGM additives seems to occur as a result of the operation of two mechanisms. The dominant mechanism is a blocking mechanism, in which the PGMs (as adatoms) block the active sites in the crystal lattice of chromium, thus preventing corrosion as described earlier. A lesser effect was also observed to occur as a result of a 'screening' mechanism, where a layer of the PGM adatoms and trapped hydrogen in the pores between the cathodic component particles partly screen the surface of the alloy, causing a decrease in the active anodic surface and in corrosion.

3. Cathodic modification of Fe–Cr stainless steels

3.1. *Addition of noble metals to Fe–Cr stainless steels*

The Tomashov group has made the main contribution to knowledge of the corrosion resistance of Fe–Cr alloys cathodically modified with noble metals in various acid media at different concentrations and temperatures.

In the early 1960s, Tomashov *et al.* [14] demonstrated the beneficial effect of the addition of platinum, palladium, rhenium, and copper to Fe–27% Cr alloys in 20 to 30% sulphuric acid at between 10 and 25° C. Even small additions (less than 0.5%) of platinum, palladium, and rhenium reduced the corrosion in the Fe–27% Cr alloy by as much as 99.85% [15]. With its higher hydrogen overvoltage, copper is less effective as a cathodic additive. The addition of 0.2% palladium to Fe–18% Cr in 20% sulphuric acid at 20° C resulted in a large increase in the corrosion resistance of the Fe–Cr alloy. Under these conditions, the corrosion resistance of Fe–18% Cr–0.2% Pd is comparable with that of an Fe–18% Cr–3% Mo alloy. When 0.2% palladium was added to Fe–25% Cr in 30% sulphuric acid at 20° C, the alloy became even more corrosion resistant than Fe–25% Cr steels with additions of either 3% molybdenum or 6% nickel. The higher corrosion resistance of an Fe–18% Cr–3% Mo–0.2% Pd steel when compared with Fe–18% Cr–0.2% Pd and Fe–18% Cr–3% Mo steels illustrated, for the first time, the synergistic beneficial effect of the simultaneous addition of molybdenum and palladium to an alloy. This effect was later confirmed by Biefer [16] and Higginson [17].

Table 1. Corrosion rate (K) of some acid-resistant alloys in 40% sulphuric acid at 100° C (after Tomashov and Chernova [18])

Alloy	*K* (*mm* y^{-1})
Fe–40% Cr	~10 000
Fe–23% Cr–28% Ni–3% Mo	3
Hastelloy A, B	0.2
C	0.3
Ti–30% Mo	0.18
Fe–40% Cr–0.2% Pd	0.05

After demonstrating the cathodic modification effect in Fe–Cr stainless steels, the Tomashov group discovered that the effect of cathodic additions was enhanced with an increasing chromium content (above 25%) in an alloy [18]. Investigations carried out on Fe–Cr alloys with varying chromium contents (25 to 100%) to which 0.2% palladium was added indicated that Fe–40% Cr–0.2% Pd had the optimum passivation characteristics in 10 to 50% sulphuric acid and 1% hydrochloric acid at 100° C. Under these conditions, the Fe–40% Cr–0.2% Pd alloy required the minimum time for self-passivation and displayed the minimum corrosion in the passive range, as well as a small critical current density and a highly negative passivation potential. The addition of 0.2% palladium to the Fe–40% Cr steel caused a dramatic decrease of a factor of 2×10^5 in the corrosion rate in a boiling solution of 40% sulphuric acid. The remarkable corrosion resistance of the Fe–40% Cr–0.2% Pd alloy when compared with other alloys can be clearly seen from Table 1.

Although the effect of the addition of palladium in improving the corrosion resistance is much less in hydrochloric acid, the corrosion rate in the passive state is still reduced by a factor of approximately 100. The alloy was found to have high corrosion rates in a solution of hydrochloric acid at concentrations of more than 1%.

This extraordinary corrosion resistance in sulphuric acid was confirmed by Higginson [19], who found that an improvement was obtained in the corrosion rate of a factor of 1 to 5×10^4 for Fe–40% Cr–0.2% Pd and Fe–40% Cr–0.2% Ru alloys compared with Fe–40% Cr in a boiling solution of 10% sulphuric acid. The alloy containing ruthenium was more resistant than the alloy containing palladium. The greater effect of the ruthemium was explained on the basis that it is a more effective cathode for the evolution of hydrogen than is palladium. A similar investigation conducted by Howarth [20] indicated that no improvement in corrosion resistance is gained by the use of platinum rather than ruthenium for purposes of cathodic modification. Higginson [17] also observed that the critical time and charge density for spontaneous passivation of Fe–40% Cr–Ru alloys depends on the concentration of ruthenium in the alloy, and the kind of acid (hydrochloric or sulphuric) in which the corrosion takes place.

Detailed investigations were carried out by Tomashov *et al.* [21] on Fe–25% Cr steels alloyed with

0.3% and 2.0% palladium and ruthenium in 5 to 50% sulphuric acid and 1 and 5% hydrochloric acid at 50 to 100° C. It was found that the general and pitting corrosion resistance were higher in the alloys containing ruthenium than in the alloys containing palladium. These results were attributed to several factors:

(a) Ruthenium reduces the overvoltage of cathodic hydrogen generation more effectively than does palladium, thereby increasing the efficiency of the cathodic process.

(b) Ruthenium, unlike palladium, reduces the rate of anodic dissolution by reducing the critical current density required for passivation, especially in media containing chloride ions. This observation was confirmed by both Biefer [16] and Higginson [17].

(c) Ruthenium is susceptible to the adsorption of oxygen and the formation of phase oxides, and thus enters the composition of the hydroxide and oxide layers formed on the surface of the steel, while palladium remains as a separate metallic phase in the surface layer.

(d) Because the passivating oxide layers on the steel contain ruthenium as well as chromium, the resistance of the steel to the activating effect of chloride ions increases. Thus, ruthenium does not impair the resistance to pitting corrosion, but palladium does impair this resistance.

An electron microscopy investigation [22] into the accumulation of palladium on the surface of Fe–25% Cr–(0.1 to 0.5%) Pd in 10% sulphuric acid at 25 to 100° C revealed that the size and amount of accumulated particles on the surface of the alloy depend not only on the initial concentration of the palladium in the alloy, but also on the temperature at which active dissolution takes place. The size and distribution of the accumulated palladium particles are explained on the basis of the theory of Erdey-Gruz and Volmer, which states that nuclei of crystallization arise at a definite supersaturation of adsorbed atoms on the surface of the alloy. An increase in the concentration of the palladium should therefore result in both an increase in the number of nuclei and a decrease in the particle size. Higginson [17] confirmed this in a study of the accumulation of ruthenium on Fe–40% Cr–(0.1 to 0.2%) Ru alloys corroding in 0.5 M sulphuric acid (4.9%) and 0.5 M hydrochloric acid (1.8%). He also found that a greater amount of accumulation occurred in a solution of hydrochloric acid than occurred in sulphuric acid, apparently as a result of the adsorption of chloride ions, which increases the surface diffusion rate of ruthenium atoms during anodic dissolution.

Biefer [16] assessed the influence of several transition metals, as well as additions of palladium and rhenium in different concentrations to type 430 ferritic stainless steel (17% Cr) in 0.5 M sulphuric acid at ambient temperature (24° C). The results indicate that the addition of 0.46% palladium to 430 stainless steel resulted in spontaneous passivation, but insufficient levels of palladium (0.06 to 0.26%) increased the active corrosion rate by a factor of as high as 10.

It was found that in 1 M hydrochloric acid (3.6%), the additions of palladium to steel 430 were strongly deleterious, and increased the corrosion rate from a factor of 10 to a factor of 30. Further, it was observed that palladium was deleterious to the pitting corrosion of ferritic stainless steels. However, at levels of 0.99% palladium, 430 stainless steel appears to have a superior corrosion resistance even to that of highly alloyed austenitic stainless steels in concentrated sulphuric acid at high temperatures.

Although Tomashov *et al.* [14] concluded that the addition of 0.2% palladium to Fe–18% Cr steel was sufficient to result in spontaneous passivation in 20% sulphuric acid at 20° C, Biefer [16] found that type 430 stainless steel with an addition of 0.26% palladium did not passivate spontaneously in 0.5 M sulphuric acid at 24° C. A probable reason for this discrepancy is the presence of relatively high amounts of carbon and impurities in the 430 stainless steel. Lizlovs and Bond [23] showed, in measurements of anodic polarization, that the performance of a standard type 430 steel was surpassed by that of a 17% chromium steel of high purity.

3.2. *Addition of noble metals to Fe–Cr–Mo stainless steels*

Tomashov *et al.* [24–26] investigated the corrosion characteristics of several Fe–Cr stainless steels containing molybdenum (2 to 3%) and palladium (0.1 to 0.5%) in sulphuric acid (1 to 80%) at temperatures varying from 10° C to boiling point (about 100° C). The results indicated that, when molybdenum is added to an Fe–25% Cr steel containing 0.3% palladium, the concentration and temperature ranges in which the steels self-passivate in sulphuric acid are narrowed.

According to them, the simultaneous alloying of Fe–25% Cr with molybdenum and palladium leads to a marked increase in the stability of the passive film in sulphuric acid, because molybdenum is incorporated in the passivating film on the steel, resulting in a more protective surface layer [24]. The shrinkage of the region of passive behaviour was also confirmed by Agarwala and Biefer [27] in their investigation of type 430 stainless steel, especially at high concentrations of sulphuric acid. They found that type 430 steels with additions of 3% Mo–0.5% Pd and 2% Mo–1% Pd have comparatively large regions of spontaneous passivity in sulphuric acid up to concentrations of 25% at temperatures near boiling point. They even passivate in the presence of 2 to 3% sodium chloride in sulphuric acid solutions at 24° C, thus showing much more resistance to chlorides than steels that contain only palladium.

The Tomashov group showed further that Fe–18% Cr–2% Mo alloyed with 0.3% palladium self-passivates, is corrosion resistant in 1 to 40% sulphuric acid at between 10 and 100° C, and has a lower corrosion rate than commercial Fe–18% Cr–10% Ni stainless steel under the same conditions [26].

Streicher [15, 28] also investigated the effect of additions of PGMs to an Fe–Cr–Mo alloy. Without these additions, the rate of attack on an Fe-28.5% Cr-4% Mo alloy in a 10% solution of boiling sulphuric acid was found to be approximately 52 000 mm per year. Each of the six added PGMs, when present in excess of a certain minimum amount that varied from 0.005 to 0.02%, passivated the Fe-28.5% Cr-4% Mo alloy in 10% boiling sulphuric acid. The minimum concentration of PGMs required to passivate the base alloy decreased with an increase in the chromium content. Additions of a PGM at a concentration lower than that required to produce passivity actually increased the corrosion rate as compared with that of Fe-28.5% Cr-4% Mo. This was also observed by Biefer [16] for Fe-17% Cr (type 430) steel.

The observation made by both Tomashov *et al.* [24] and Agarwala and Biefer [27] that the simultaneous presence of palladium and molybdenum in Fe-Cr steels promotes more stable passivity than the presence of each individual element alone was confirmed by both Streicher [15, 28] and Higginson [17]. Higginson found that Fe-40% Cr that had been alloyed with both 1.8% molybdenum and 0.1% ruthenium passivated far more quickly in sulphuric acid (0.5 M) than did an Fe-40% Cr-0.1% Ru alloy. According to Tomashov *et al.* [24] this is true not only for solutions of sulphuric acid, but also for solutions of dilute hydrochloric acid (1 to 3%). However, Higginson [17] showed that the addition of 0.1% ruthenium to an Fe-40% Cr-1.8% Mo steel could not cause the spontaneous passivation of the alloy to occur in a solution of 0.5 M hydrochloric acid. The fact that Tomashov *et al.* could achieve spontaneous passivation while Higginson could not, can be attributed to different conditions in their respective investigations.

The addition of molybdenum has different effects on the corrosion resistance of chromium steels in the active state in solutions of sulphuric and hydrochloric acid. In solutions of sulphuric acid, the presence of molybdenum reduces the corrosion rate, but in solutions of hydrochloric acid, it increases the rate. The corrosion potential in both acids of steel containing molybdenum is more positive than that of steel without molybdenum. This fact can be explained if it is assumed that molybdenum not only retards anodic dissolution, but also increases the effectiveness of the cathode process owing to the reduced overvoltage of hydrogen on molybdenum. The predominant action of molybdenum on the anodic process appears in solutions of sulphuric acid but, in hydrochloric acid, where passivation is hindered by the presence of chloride ions, it is mainly the cathodic influence of molybdenum that prevails. This leads to a marked increase in the rate of dissolution of steel, because the effectiveness of the cathodic process on molybdenum in hydrochloric acid is insufficient to bring the steel into the passivated state. The simultaneous presence of palladium and molybdenum in steel produces a more effective cathodic process [24], and could possibly lead to passivation. Thus, in sulphuric acid, molybdenum affects not only the cathodic process (together with PGMs), but also retards the anodic process. The combined influence of molybdenum and PGMs on the anodic and cathodic processes of Fe-Cr stainless steel in sulphuric acid is summarized schematically in Fig. 3. Streicher [28] also carried out investigations into the pitting corrosion of Fe-28% Cr-4% Mo alloys to which PGMs in several halide media had been added. These results are summarized in Table 2, together with comparative data for some other alloys.

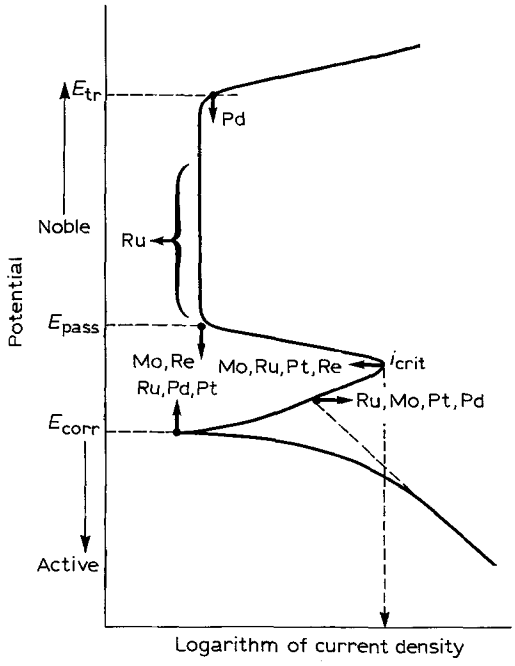

Fig. 3. Summary of the effects of alloying additions on the polarization characteristics of Fe-Cr stainless steel in sulphuric acid.

The results show clearly that palladium destroys the pitting resistance in all of the three pitting solutions tested, while rhodium impairs the resistance in ferric chloride and the bromine-bromide solution. None of the other four PGMs had any influence on the pitting resistance in these media, except for platinum, which caused failure in the bromine-bromide solution. No mechanism was suggested as an explanation for these observations. Streicher concluded that, of the six PGMs only iridium, osmium, and ruthenium can be used to produce the passivity of stainless steels in sulphuric acid without impairing their resistance to pitting corrosion in oxidizing chloride and bromide environments.

As far as organic media are concerned, it was found [14] that the addition of 0.1% palladium to Fe-25% Cr in a solution of 50% formic acid at 100° C decreased the corrosion rate of steel by a factor of approximately 60. An Fe-25% Cr-3% Mo steel is stable under these conditions, both with and without palladium.

4. Cathodic modification of Fe-Cr-Ni stainless steels

Although the effect of cathodic alloying additives on Fe-Cr-Ni stainless steels is not as dramatic as for Fe-Cr steels, it can nevertheless bring about marked improvement in the corrosion resistance of Fe-Cr-Ni alloys, especially in fairly aggressive conditions [29].

Table 2. Comparison of results for investigations of pitting resistance in halide media [15]

Alloy	*Permanganate chloride* at 90° C*	*Ferric chloride† at 40° C*	*Bromine-bromide at room temp.‡*	*Sodium hypochlorite at room temp.§*
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	–
Re–28% Cr–4% Mo + Os	R	R	R	–
Re–28% Cr–4% Mo + Ru	R	R	R	R

R = Resistant; F = Fails.

* 2% $KMnO_4$–2% NaCl.

† 10% $FeCl_3 \cdot 6H_2O$, with crevices.

‡ 54.5% Br_2 + 20.6% $ZnBr_2$.

§ 0.1% NaClO with Teflon crevices.

4.1. *Addition of noble metals to Fe–Cr–Ni stainless steels*

The addition of 0.1 to 0.5% platinum, 0.1 to 0.9% palladium, and 1.2% copper to Fe–18% Cr–9% Ni (an austenitic stainless steel) in 20 to 40% sulphuric acid at 20° C reduced the corrosion of the Fe–Cr–Ni alloy by as much as 99.85% [15, 30]. The results also indicated that the effectiveness of the alloying additions increased in the order Cu < Pd < Pt.

An electrochemical investigation into the alloying of Fe–25% Cr–6% Ni steel with palladium [31] (0.1, 0.2, and 0.5%) showed that the corrosion rate is reduced by more than an order of magnitude in 20% sulphuric acid at 100° C over that for steel without palladium. However, steels containing palladium (0.1 to 0.5%) do not reach the stable passive region, and continue to dissolve at a considerable rate. The corrosion rate of Fe–25% Cr–6% Ni–0.5% Pd in a solution of 10% sulphuric acid at 100° C is lower by a factor of 4 compared with the steel without any palladium.

Tomashov [14] also demonstrated that the addition of 0.2% palladium to an Fe–18% Cr–10% Ni alloy greatly reduced the corrosion of this austenitic stainless steel. The substitution of part of the nickel by manganese (Fe–18% Cr–2% Ni–8% Mn) produced an austenitic stainless steel with a corrosion performance that was not nearly as good as that of a steel with 10% nickel. The alloying of this manganese-substituted steel with 0.2% palladium rectified this impaired corrosion resistance, and resulted in a steel with similar corrosion characteristics to that of an Fe–18% Cr–10% Ni–0.2% Pd alloy.

A recent study by Peled and Itzhak [32] into the effect of silver, palladium, and gold on the corrosion behaviour of hot-pressed and sintered type 316 stainless steel in 0.5 M sulphuric acid at 25° C indicated that the corrosion resistance of the base alloy could be dramatically improved by additions of noble metals. Silver concentrations of less than or equal to 1% improved the corrosion resistance of the sintered stainless steel only for limited periods of exposure. Platinum additions of about 2% were found to be sufficient to preserve the sintered stainless steel in the passive state. However, high platinum contents (about 5%) resulted in a tendency for the passive layer to break down. Samples containing additions of gold at various concentrations (1 to 5%) exhibited clear anodic active–passive transitions with a wide range of passivation. The addition of 5% gold to the sintered stainless steel caused the alloy to remain passive.

An interesting beneficial synergistic effect between nickel and ruthenium was noticed by Streicher [28]. Lower concentrations of ruthenium (0.1%) and nickel (0.1%) were needed to passivate Fe–28% Cr–4% Mo in a 10% solution of boiling sulphuric acid than the concentrations of either ruthenium (0.02%) or nickel (0.25%) that were needed when they were used alone. Although it seemed that Higginson [17] was unaware of this since he neither confirmed nor disproved it; he nonetheless found that the addition of 1% nickel to an Fe–40% Cr–0.1% Ru alloy resulted in an increase in the time needed for the occurrence of spontaneous passivation in 0.5 M sulphuric acid. He also concluded that the inhibition of the anodic dissolution reaction in sulphuric acid was much greater for the alloy containing both nickel and ruthenium than for that containing only 0.1% ruthenium. The alloying of Fe–40% Cr–0.1% Ru with 1% nickel also caused spontaneous passivation to occur approximately seven times faster in 0.5 M hydrochloric acid than for the Fe–40% Cr–0.1% Ru alloy. Thus, while an addition of 1% nickel to Fe–40% Cr–0.1% Ru was advantageous and lowered the passivation time in hydrochloric acid, the same did not apply when sulphuric acid was used, since the passivation time increased.

As far as organic acid media are concerned, work by the Tomashov group [14, 30] indicated that an Fe–25% Cr–6% Ni–0.1% Pd alloy in a solution of 50% formic acid at 100° C had a significantly reduced rate of corrosion when compared with the alloy without palladium. An alloy of 26% Cr–0.5% Ni to which noble metals had been added (0.5% platinum, 0.5 to 1.0% palladium) could withstand solutions of 50% formic acid and 10% oxalic acid at 100° C far better than a similar alloy without the additions of any noble metals.

4.2. *Addition of noble metals to Fe–Cr–Ni–Mo and Fe–Cr–Mn–Ni stainless steels*

Investigations by Tomashov *et al.* [14, 29, 33, 34] into the corrosion resistance of nitrided stainless steels revealed that an addition of 3% molybdenum to Fe–25% Cr–6% Ni steel in a solution of 30% sulphuric acid at 20° C produced a sufficiently stable alloy in which the further addition of palladium (0.1%) did not result in any significant improvement in the corrosion resistance [29]. This occurs as a result of the fact that molybdenum not only retards the anodic dissolution of steel, but also promotes the cathodic evolution of hydrogen. Passivation, is thus caused by the increased effectiveness of the cathodic process as well as the inhibition of the anodic process.

The work of the Tomashov group also showed that highly nitrided (0.7 to 0.9%) Fe–25% Cr–3% Ni–2% Mo–Mn stainless steels to which 0.1 to 0.5% palladium had been added had a very high corrosion resistance in mildly aggressive conditions, such as in solutions of 20 to 40% sulphuric acid at 20 to 100° C, as well as in solutions of 1 to 3% hydrochloric acid at 20 to 50° C [34]. However, at least 0.2% palladium is needed for self-passivation and high corrosion resistance to occur under more aggressive conditions (2% or higher hydrochloric acid at 50° C or higher, and 30% or more sulphuric acid at 50° C or higher [29]). In mildly aggressive media, the corrosion resistance of the steel depends on the ability of the molybdenum to cause self-passivation as a result of the increased effectiveness of the cathodic process and inhibition of the anodic process. The simultaneous addition of palladium and molybdenum in a stainless steel broadens the region of self-passivation of the steel. The favourable influence of palladium on the corrosion resistance of stainless steel is due primarily to the cathodic modification of the steel and, in the presence of molybdenum, to its beneficial effect on the stability of the passive state.

Results also indicated that Fe–25% Cr–6% Ni–3% Mo–0.2% Pd that does not contain nitrogen could not be passivated in a solution of hydrochloric acid. Only a high nitrogen content (0.5% or more) leads to an increase in the corrosion resistance and self-passivation of these alloys in solutions of dilute hydrochloric acid (2 to 5% hydrochloric acid at 50° C) [33]. The positive influence of nitrogen occurs as a result of its influence on the structure of steel. A high nitrogen content creates a more homogeneous austenitic structure, and thus prevents the partitioning of chromium, molybdenum, and nickel in a two-phase austenitic–ferritic structure. Steel containing palladium but no nitrogen cannot be passivated in solutions of hydrochloric acid, apparently owing to the heterogeneity of the structure, which contains approximately 40% ferrite. The presence of appreciable amounts of both austenite and ferrite phases in the alloy, which cause a galvanic interaction between the two electrochemically different phases, is possibly responsible for this observed corrosion behaviour.

Tomashov *et al.* [34] proved that Fe–Cr–Ni–Mn and Fe–Cr–Mn alloys containing 0.5% palladium self-passivated, and had a high corrosion resistance in solutions of 20% sulphuric acid at 100° C. However, the steels containing only 0.2% palladium did not self-passivate in solutions of 2 and 3% hydrochloric acid at 25° C, and had a low resistance to corrosion. Manganese shifts the complete passivation potential of Fe–Cr steel to values that are more positive, but to a lesser degree than nickel. The beneficial effect obtained when chromium steels are alloyed with nickel and manganese can be ascribed to the fact that they cause a smaller shift in potential to the positive direction upon complete passivation than occurs when they are alloyed with nickel alone. The further addition of nickel to Cr–Mn steels also lowers the critical current density at the onset of passivation. This permits better self-passivation, and a higher corrosion resistance upon cathodic alloying.

4.3. *Galvanic coupling in Fe–Cr–Ni stainless steels*

Bianchi *et al.* [35] investigated the galvanic coupling of different stainless steels with sheet platinum in various non-oxidizing acid solutions at various concentrations and temperatures. For example, it was found that, in an aerated solution of 38% sulphuric acid at 25° C, types 316, 304, and 430 (a ferritic alloy) stainless steel resisted corrosion when the ratio of the area of platinum to that of the stainless steel was 1, 10, and 100, respectively. This acquired corrosion resistance was attributed to the anodic protection of the stainless steel by platinum, which is a more efficient cathode for the reduction of oxygen. This greater efficiency of platinum for the reduction of oxygen shifted the potential of the stainless steel to a value in the passive range, thereby enhancing the resistance to corrosion. The same effect is observed when the platinum is alloyed with the steel, and is known as cathodic modification of the stainless steel by the PGM. The galvanic coupling of two austenitic stainless steels, AISI 304 (18% Cr–8% Ni) and AISI 316 (18% Cr–8% Ni–2% Mo) with platinum, was studied electrochemically by Kabi *et al.* [36] in solutions of 2 and 5 M sulphuric acid at 28° C. They confirmed that galvanic coupling with platinum enhanced the corrosion resistance of both steels, since the critical current density was lowered at the onset of passivation, as was the passivating current density. The corrosion potential of both alloys also shifted to a more positive value.

5. Cathodic modification of duplex stainless steels

The development of duplex stainless steels (steels containing a ferrite–austenite mixture) was first reported by Bain and Griffiths [37] as early as 1927. Duplex stainless steels combine the advantages of ferritic and austenitic stainless steels and, although a large amount of data has been collected and published about duplex stainless steels, very little work has been reported in the literature about the addition of noble metals to these steels.

It would appear that Tomashov's is the only group that has carried out any work on the influence of the addition of noble metals on duplex stainless steels. Furthermore, it appears that their work on the addition of palladium to duplex stainless steels was purely incidental, their main thrust having been focused on the investigation of the effect of palladium on the corrosion characteristics of highly nitrided austenitic stainless steels (some containing molybdenum as well) in non-oxidizing acid solutions. The occurrence of two phases (ferrite and austenite) in some highly nitrided austenitic stainless steels also led to investigations of duplex stainless steels that were alloyed with palladium [34].

In one of the investigations by the Tomashov group [33] into the corrosion resistance of Fe–Cr–Ni stainless steels in hydrochloric acid, two duplex stainless steels were produced with low levels of nitrogen (0.03% or more). The Fe–25% Cr–6% Ni–3% Mo alloy contained a 30% ferritic phase, while the Fe–25% Cr–6+ Ni–3% Mo–0.2% Pd alloy contained a 40% ferrite phase. Both steels were found to corrode actively in a solution of 3% hydrochloric acid at 50° C.

A higher corrosion rate was found in the duplex steel containing palladium because, in conditions in which the steel does not self-passivate and in which it corrodes with the evolution of hydrogen, the presence of an effective cathodic additive with a low hydrogen overvoltage enhances the cathodic reaction and increases the corrosion rate.

This investigation showed that duplex stainless steels containing palladium cannot be passivated in a solution of up to 3% hydrochloric acid at 50° C because of the heterogeneity of its structure. Both chromium and molybdenum are powerful ferrite stabilizers, while nickel is primarily an austenite stabilizer. Therefore, the distribution of the different components in the two phases differs by several percentage points as a result of partitioning. The austenitic phase, being depleted of chromium and molybdenum and enriched with nickel, experienced difficulty in achieving passivation.

In another paper on the corrosion resistance of highly nitrided austenitic stainless steels alloyed with palladium, Tomashov *et al.* [34] produced some duplex stainless steels that typically consisted of 18 to 25% chromium, 7 to 11% manganese, approximately 2% molybdenum, and nearly 1% nitrogen, with a varying ferrite content of 36 to 50%. These steels were additionally alloyed with 0.1 to 0.5% palladium. No nickel was present in any of these alloys.

Corrosion tests conducted in solutions of 20 to 50% sulphuric acid at 20 to 100° C indicated that all the duplex alloys containing palladium initially corroded intensively after immersion and activation before they became self-passivated. The time required for self-passivation decreased with an increase in both the palladium content of the steel and an increase in temperature, but increased with an increase in the concentration of acid (20 to 40% sulphuric acid). In a solution of 20% sulphuric acid at 100° C, only the steels containing 0.4 and 0.5% palladium self-passivated. This investigation also showed that duplex stainless steels containing palladium have a greater corrosion resistance in 2 to 3% hydrochloric acid at 20 to 50° C than did similar cathodically modified austenitic stainless steels.

6. Cathodic modification of titanium and titanium-based alloys

Stern and Wissenberg [38] carried out a systematic study of the corrosion resistance of titanium alloyed with various PGMs. The most effective metals were found to be platinum, ruthenium, and palladium. The addition of 0.44% palladium to titanium lowered the rate of corrosion by a factor of 100 in a boiling solution of 10% sulphuric acid. Reductions in the corrosion rate of a similar magnitude were also found in solutions of boiling 3 and 10% hydrochloric acid. The addition of PGMs to titanium was not found to be detrimental to its resistance to corrosion in highly oxidizing media (nitric acid, ferric chloride). This occurs because titanium does not display a transpassive region.

Cotton [39] showed that, even at concentrations as low as 1%, additions of palladium to titanium take the form of the intermetallic compound Ti_2Pd. This contrasts with the situation for stainless steels and chromium-based alloys, where the PGM is present in solid solution. Cotton suggested that the intermetallic compound dissolves in the electrolyte before the onset of passivation, and that palladium is then reprecipitated onto the surface in an elemental form from the solution. The observation that the corrosion of titanium in non-oxidizing acids can be greatly reduced by the addition of a small quantity of a soluble palladium salt suggests this mechanism. Cotton and Green [40] further suggested that this implies that spontaneous passivation of titanium–palladium will be facilitated by stagnant conditions rather than by conditions of dynamic flow.

However, the prevailing weight of opinion from more recent studies of cathodic modification is that a process of surface diffusion, rather than a dissolution–deposition process, is responsible for the redistribution of PGMs before the onset of passivation. Armstrong *et al.* [41] used the ring–disc electrode technique in conjunction with scanning electron microscopy to investigate the corrosion of a Ti–0.2% Pd alloy. The decrease in the rate of corrosion prior to passivation was accompanied by the accumulation of loosely adherent palladium particles (approximately 0.025 μm in size) on the surface of the alloy. The rate at which the inhibition of corrosion was established was extremely dependent upon the degree of forced diffusion, since this affected the concentration of free palladium at the surface of the alloy. There was no evidence to suggest that the palladium species in solution played any part in the process of corrosion inhibition.

7. Surface alloying with platinum-group metals

Unlike bulk alloying which requires the introduction of a considerable amount of a noble-metal component to obtain a protective effect, surface alloying seems to be a more economical way to achieve the same purpose. It is therefore not surprising that a fair amount of research has been conducted to establish the corrosion resistance of various alloys with PGM surface coatings.

7.1. *Cathodically modified chromium coatings*

Tomashov *et al.* [42] showed that the corrosion resistance of electrolytic chromium plating should be substantially increased in solutions of non-oxidizing acids when chromium and palladium were deposited layer-by-layer. Small additions of palladium (1 to 3%) significantly increased the corrosion resistance of chromium coatings in solutions of 20% sulphuric acid and 5 to 10% hydrochloric acid. The sequence of alternating chromium and palladium layers, as well as subsequent heat treatment (annealing) after plating, also influenced the corrosion characteristics.

7.2. *Surface alloying in Fe–Cr alloys*

When Fe–27% Cr is surface alloyed with palladium (0.1 to 0.5 μm) by electroplated coating followed by annealing, it acquires a high resistance to corrosion in solutions of 20% sulphuric acid at 100° C [43–45]. While steel that does not contain palladium was non-resistant, the corrosion rate in the coated steel decreased by several orders of magnitude. The annealing of the samples did not hinder the corrosion resistance, despite the diffusion of a considerable amount of palladium into the base metal. In milder conditions, the introduction of less palladium into the surface layer is even sufficient to prevent corrosion. It was calculated [44] that the minimum amount of palladium that is necessary per unit surface area to impart corrosion resistance is about 0.1 $\mathrm{g\,m^{-2}}$, which corresponds to a mean palladium layer thickness of approximately 10 nm.

The electrospark method of coating [43–45] yields similar results for corrosion resistance in Fe–27% Cr, and may offer a convenient method for increasing the corrosion resistance of large structures that cannot be electroplated with palladium in baths.

Agarwala and Biefer [27] agree with the Tomashov group that the surface deposition of palladium appears to be a relatively inexpensive way of obtaining good corrosion resistance in stainless steels. They found that the deposition of palladium from a palladium chloride solution on type 430 stainless steel and type 430 stainless steel plus 2% molybdenum caused the specimens to passivate spontaneously when exposed to 0.5 M sulphuric acid. The molybdenum-bearing steel was more readily passivated than the molybdenum-free steel. They concluded that this behaviour supports statements that palladium enriched the surface of an alloy during the initial period of corrosion.

7.3. *Surface alloying in Fe–Cr–Ni stainless steels*

Work on the cathodic alloying of Fe–Cr–Ni stainless steel surfaces was first carried out by Bianchi *et al.* [46] who electroplated an Fe–19% Cr–11% Ni alloy with platinum. They concluded that, even with a platinum coverage of as low as 20 $\mathrm{mg\,m^{-2}}$, the platinum provides efficient protection of the stainless steel in solutions of concentration up to 75% H_2SO_4 at 25° C. They attributed this greater corrosion resistance of the stainless steel to two factors. Firstly, platinum is a more efficient cathode for the reduction of oxygen than is stainless steel and, secondly, the selective deposition of platinum in the form of small round particles (approximately 0.01 μm in diameter) blocked the most active sites of the stainless steel surface. Electron microscopy was carried out on thin-film samples, and provided evidence for the selective electrodeposition of platinum at emerging dislocations and grain boundaries.

Tomashov *et al.* [43, 47] investigated this possibility using two different methods of applying palladium to the surface of an Fe–18% Cr–10% Ni alloy, namely electrolytic plating, and electrospark alloying. The Fe–18% Cr–10% Ni alloy with electrolytically deposited coatings of palladium (0.1 to 5 μm) acquired high corrosion resistance in a solution of 20% sulphuric acid at 100° C. Under less aggressive conditions, even less palladium is required in the surface layer to protect the steel from corrosion. When the Fe–18% Cr–10% Ni stainless steel was modified by electrospark alloying, stable passivity was once again obtained. When an Fe–40% Cr–0.2% Pd alloy was used for the coating, the concentration of palladium on the surface of the Fe–18% Cr–10% Ni steel was approximately 1%, which increased to between 12 and 18% as self-passivation was established. It was found that spark alloying with this combined chromium and palladium alloying addition produced better resistance against corrosion than that obtained when alloying was carried out with palladium alone. However, electrolytic deposition produced a smoother, more continuous coating than was produced by spark alloying.

In acid solutions (20% H_2SO_4 at 100° C), the simultaneous presence of a specimen of carbon steel, which dissolves with the evolution of hydrogen, causes the potential of the specimen coated with palladium (1 μm) to shift towards a more negative value, and causes the stainless steel to dissolve actively. This situation arises irrespective of whether or not there is contact between the carbon steel and the stainless steel coated with palladium.

7.4. *Surface alloying in titanium alloys*

Tomashov *et al.* [45] found that the corrosion resistance of titanium in solutions of sulphuric acid (20 to 40%) and hydrochloric acid (5 to 10%) at 100° C can be substantially increased if the titanium surface is plated galvanically with palladium (1 to 20 μm), both with and without subsequent annealing.

Early electrochemical work carried out by Tomashov *et al.* [48] on titanium–palladium alloys showed that a 2% concentration of palladium gave the optimum resistance to corrosion. However, in solutions of hydrochloric and sulphuric acids, a large effect still occurred at a concentration of 0.1% palladium. This work eventually led to the development of a commercial titanium–palladium alloy containing 0.2% palladium. Tomashov *et al.* [49] have also demonstrated that titanium and titanium–palladium alloys are passivated more easily when titanyl ions (TiO^{2+}) or dissolved oxygen are present in the solution. Their presence was shown to cause an increase in the rate of the cathodic process. The addition of palladium to high-strength titanium alloys [50] (containing aluminium and molybdenum) has also been shown not only to cause spontaneous passivation in non-oxidizing acids, but also to reduce the tendency of the alloys to oxidation at elevated temperatures.

In comparison with the amount of reported work on titanium–palladium alloys, there is very little reported work on equivalent titanium–ruthenium alloys. Tomashov *et al.* [51] made a comparative analysis of the influence of ruthenium and palladium on the corrosion resistance of titanium in non-oxidizing acids. The corrosion rates of titanium–ruthenium alloys fell continuously with an increase in the concentration of ruthenium up to 2%. The effect was more pronounced in solutions of weaker acid. The results confirmed that ruthenium is a more effective cathode for the evolution of hydrogen than is palladium. A Ti–8% Ni–0.2% Ru alloy has been shown to be suitable for use as a corrosion-resistant anode in neutral and weakly acidic chloride-containing solutions [52].

McCafferty and Hubler [53] showed that the active dissolution of titanium in a solution of boiling 1 M sulphuric acid is reduced by three orders of magnitude when 1.8 g cm^{-2} palladium is ion-implanted into a thin surface layer. The ion-implantation method of alloying for titanium–palladium is of special interest in that ion-implanted palladium does not take the form of an intermetallic compound. Using the Rutherford backscattering technique it was shown that the palladium is initially buried beneath the surface. The preferential dissolution of titanium during active dissolution causes a redistribution of the palladium until a high surface concentration ($\sim$20%) is obtained.

The technique of ion-implantation was also used by Appleton *et al.* [54] to produce alloys implanted with titanium–platinum. Surface analysis by use of ion-scattering measurements again revealed a large-scale surface migration of platinum during anodic dissolution of the alloy. Appleton *et al.* also suggested that some of the platinum on the surface underwent a transition from 'active' (*i.e.* hydrogen evolving) to 'inactive' (*i.e.* non-hydrogen evolving) during the course of this migration. A possibility, also raised by the Tomashov group, is that electrical contact was lost between the 'inactive' platinum and the alloy substrate.

The main features of the influence of noble-metal additions on the corrosion resistance of the various alloy systems are summarized in Table 3.

8. Conclusions

From the above discussion, it can be concluded that cathodic alloying additives (PGMs) greatly increase the corrosion resistance of chromium in non-oxidizing acid environments. The processes of active dissolution and passivation of cathodically modified chromium can be satisfactorily interpreted from a comparison of the different electrochemical processes: the anodic process on chromium, and the process on the cathodic component.

It is also evident that the corrosion resistance of Fe–Cr stainless steels can be significantly increased in non-oxidizing media over a large range of concentrations and temperatures by small additions (0.5% or less) of PGMs. The amount of PGMs needed to produce passivity in Fe–Cr alloys can be decreased by an increase in the chromium content. When molybdenum is also present in the base alloy, a further beneficial synergistic effect between molybdenum and the PGMs can decrease the concentration of the PGMs needed for stable passivity even further. The pitting corrosion resistance of Fe–Cr–Mo steels can be impaired by some of the PGMs. The use of various methods for surface alloying has also proved successful in reducing high corrosion rates, and similar results to those achieved by use of bulk alloying can be achieved in increasing the resistance to corrosion. However, long-term assessment has to be carried out on surface alloying before any conclusive judgement can be reached.

Similarly, the alloying of multicomponent stainless steels with palladium can also lead to a significant increase in the corrosion resistance of such steels, especially in more aggressive environments. However, the corrosion resistance of these steels also depends, to a large extent, on the presence and combination of other components, e.g. molybdenum, manganese, and nitrogen.

Although the work carried out by Tomashov *et al.*

Table 3. Main features of the influence of noble metal additions on the corrosion resistance of various alloy systems

Alloy system	H_2SO_4	*HCl*
Ductile chromium	5–98% at boiling point	5–15% at boiling point
	0.1% PGM additions cause a decrease in the corrosion rate by a factor of 10^5 or more. Decreasing order of effectiveness of PGMs: Ir > Rh > Ru > Pt > Pd > Os.	
Ferritic stainless steels	20–30% at 25° C. Additions of $<0.5\%$ PGMs decrease the corrosion rate by as much as 99.85%.	
	Synergistic beneficial effect on corrosion rate if both a PGM and Mo are present in an alloy. Effect of PGM on corrosion rate increase with increasing chromium content (above 25%) in an alloy. Fe–40% Cr–0.2% Pd even more resistant than Hastelloy alloys in	
	10–50% at boiling point	1% at boiling point
	Ru a better cathodic additive than Pd. Insufficient cathodic additive accelerates corrosion.	
	Behaviour of PGM alloyed ferritic SSs different in H_2SO_4 and HCl media.	
Austenitic stainless steels	Effect of PGM additions not as dramatic as for ferritic stainless steels, but increase corrosion resistance nonetheless, especially in fairly aggressive conditions. Synergistic beneficial effect on corrosion rate if both a PGM and nickel are present in an alloy. Also possible to enhance corrosion resistance by galvanic coupling with Pt.	
Duplex stainless steels		3% at 50° C. Alloys with low nitrogen content corrode actively even with PGM additions.
	20–50% at 20–100° C	2–3% at 20–50° C
	PGM additions (0.5%) cause self-passivation	Highly nitrided manganese substituted duplex SSs with PGM additives more resistant than similar cathodically modified austenitic SS
Titanium-based alloys	10% at 100° C	3–10% at 100° C
	PGM additions substantially increase corrosion resistance. Corrosion rates lower by a factor of 100. Commercial alloy with 0.2% Pd developed.	

[33, 34] provides some insight into the corrosion behaviour of cathodically modified duplex stainless steels, there are still many questions that need to be answered. It is not clear how the cathodically modified duplex stainless steels that contain nickel will behave in solutions of sulphuric and hydrochloric acids, and how this behaviour will compare with the results found for Fe–Cr–Mo–Mn–Pd duplex alloys. The influence of PGM additions also needs to be more thoroughly and extensively investigated and quantified. The effect of the addition of PGMs on the corrosion mechanism and the corrosion of each phase also needs clarification. Work on this has already started in the Physical Metallurgy Division of Mintek.

As is the case for chromium and stainless steels, the corrosion resistance of titanium and titanium-based alloys can be increased in reducing environments by the addition of PGMs to titanium and its alloys. Because titanium does not display a transpassive region, the addition of PGMs to titanium is not detrimental to its corrosion resistance in highly oxidizing media. This is in contrast to chromium and stainless steels, where the addition of PGMs accelerates corrosion in highly oxidizing media.

The addition of palladium to titanium resulted in the formation of an intermetallic compound, Ti_2Pd, contrary to the situation for stainless steels and chromium-based alloys, where the palladium is present in solid solution. However, evidence indicates that, for all cathodically modified alloys of titanium, stainless steel, and chromium, there is an enrichment of the PGMs on the surface of the alloy at the onset of passivation. It seems that, in all cases, the enrichment of the surface of the alloy during the corrosion process can be explained as being due to a diffusion mechanism.

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References

[1] J. H. Potgieter, A. M. Heyns and W. Skinner, *J. Appl. Electrochem.* **20** (1990) 711-5.

[2] N. D. Tomashov, G. P. Sinelshchikova and M. A. Vedeeva, *Dokl. Akad. Nauk. SSSR* **62** (1948) 105-8.

[3] N. D. Thomashov and G. P. Chernova, 'Passivity and protection of metals against corrosion', Nauka, Moscow (1965) and translated from Russian by B. H. Tytell, Plenum Press, New York (1967) pp. 89-97.

[4] M. Stern and H. Wissenberg, *J. Electrochem. Soc.* **106** (1959) 755-59.

[5] N. D. Greene, C. R. Bishop and M. Stern, *ibid.* **108** (1961) 836-41.

[6] N. D. Tomashov, G. P. Chernova and E. N. Ustinskii, *Platin. Met. Rev.* **23** (1979) 143-49.

[7] N. D. Tomashov, G. P. Chernova, V. I. Trevilov, A. N. Ratinski, N. E. Poryadchenko, E. F. Savranski and E. N. Ustinskii, *Prot. Met.* **16** (1980) 208-13.

[8] *Idem, ibid.* **19** (1983) 89-93.

[9] N. D. Tomashov, G. P. Chernova and E. N. Ustinskii, *ibid.* **16** (1980) 452-55.

[10] N. D. Tomashov, *ibid.* **22** (1986) 685.

[11] N. D. Tomashov, G. P. Chernova and E. N. Ustinskii, *Corrosion* **40** (1984) 134-38.

[12] *Idem, Prot. Met.* **17** (1981) 325-30.

[13] N. D. Tomashov, G. P. Chernova, E. N. Ustinskii, A. E. Chalykh, M. I. Il'in, V. V. Matveev and A. E. Rubtsov, *ibid.* **20** (1984) 158-62.

[14] Tomashov, N. D., *Werkstoffe und Korrosion* **8** (1967) 694-707.

[15] M. A. Streicher, *Platin. Met. Rev.* **21** (1977) 51-5.

[16] G. J. Biefer, *Can. Metall. Q.* **9** (1970) 537-50.

[17] A. Higginson, 'The passivation of Fe-Cr-Ru alloys in acidic solutions', Ph.D. thesis, University of Manchester (1987).

[18] N. D. Tomashov and G. P. Chernova, *Prot. Met.* **11** (1975) 379-84.

[19] A. Higginson, Private communication. Randburg, Council for Mineral Technology (1984).

[20] D. Howarth, Private communication. Randburg, Council for Mineral Technology (1987).

[21] N. D. Tomashov, G. P. Chernova, L. A. Chigirinskaya and E. A. Nasedkina, *Prot. Met.* **22** (1986) 704-10.

[22] N. D. Tomashov, G. P. Chernova, L. N. Volkov, A. P. Zakharov and Z. E. Sheshenina, *ibid.* **9** (1973) 289-92.

[23] E. A. Lizlovs and A. P. Bond, *J. Electrochem. Soc.* **116** (1969) 574.

[24] N. D. Tomashov, G. P. Chernova, S. A. Golovanenko, E. A. Ul'yanin and A. D. Goronkova, *Prot. Met.* **16** (1980) 83-9.

[25] N. D. Tomashov, G. P. Chernova and O. N. Markova, *ibid.* **9** (1973) 616-18.

[26] N. D. Tomashov, G. P. Chernova, A. V. Ryabchenkov, V. I. Gerasimov, L. I. Aksenova, O. D. Agakishiev and L. A. Chigirinskaya, *ibid.* **21** (1985) 155-59.

[27] V. S. Agarwala and G. J. Biefer, *Corrosion* **28** (1972) 64-74.

[28] M. A. Streicher, *ibid.* **30** (1974) 77-91.

[29] N. D. Tomashov, G. P. Chernova and L. A. Chigirinskaya, *ibid.* **34** (1978) 445-46.

[30] T. P. Hoar, *Platin. Met. Rev.* **2** (1958) 117-19.

[31] N. D. Tomashov, G. P. Chernova and L. N. Volkov, *Prot. Met.* **6** (1970) 388-90.

[32] P. Peled and D. Itzhak, *Corros. Sci.* **28** (1988) 1019-28.

[33] G. P. Chernova, L. A. Chigirinskaya and N. D. Tomashov, *Prot. Met.* **16** (1980) 1-5.

[34] N. D. Tomashov, G. P. Chernova, V. I. Lakomskii, G. F. Torkhov, L. A. Chigirinskaya and V. A. Slyshankova, *ibid.* **13** (1977) 6-11.

[35] G. Bianchi, A. Barosi and S. Trasatti, *Electrochim. Acta* **10** (1965) 83-95.

[36] C. Kabi, K. P. Mukherjee and M. C. Rastogi, *J. Electrochem. Soc. India* **34** (1985) 256-60.

[37] E. C. Bain and W. E. Griffith, *Trans. Metall. Soc. AIME* **75** (1927) 166-213.

[38] M. Stern and H. Wissenberg, *J. Electrochem. Soc.* **106** (1959) 759-64.

[39] J. B. Cotton, *Platin. Met. Rev.* **11** (1967) 50-2.

[40] J. B. Cotton and M. L. Green, *Proceedings of the Third International Conference on Metallic Corrosion* **1** (1966) 215-33.

[41] R. D. Armstrong, R. E. Firman and H. R. Thirsk, *Corros. Sci.* **13** (1973) 409-20.

[42] N. D. Tomashov, G. P. Chernova and T. A. Fedoseeva, *Prot. Met.* **12** (1976) 1-3.

[43] N. D. Tomashov, G. P. Chernova, T. A. Fedoseeva and L. P. Kornienko, *ibid.* **17** (1981) 406-11.

[44] N. D. Tomashov, G. P. Chernova, S. M. Reshetnikov, T. A. Fedoseeva, S. F. Vdovin and L. P. Kornienko, *ibid.* **15** (1979) 525-28.

[45] N. D. Tomashov, G. P. Chernova and T. A. Fedoseeva, *Corrosion* **36** (1980) 201-7.

[46] G. Bianchi, G. A. Camona, G. Fiori and F. Mazza, *Corros. Sci.* **8** (1968) 751-57.

[47] N. D. Tomashov, G. P. Chernova, T. A. Fedoseeva and L. P. Kornienko, *Surf. Tech.* **13** (1981) 241-56.

[48] N. D. Tomashov, G. P. Chernova and R. M. Altrovsky, *J. Electrochem. Soc.* **108** (1961) 113-19.

[49] N. D. Tomashov, G. P. Chernova and T. V. Chukalovskaya, *Prot. Met.* **7** (1971) 589-91.

[50] N. D. Tomashov, G. P. Chernova, N. F. Anoshkin, S. V. Moroznikova, E. I. Oginskaya and Yu. S. Ruskol', *ibid.* **9** (1973) 594-97.

[51] N. D. Tomashov, G. P. Chernova, T. V. Chukalovskaya, G. M. Plavnik, R. I. Nazarova, A. P. Zakharov and Z. E. Sheshenina, *ibid* **8** (1972) 174-77.

[52] N. D. Tomashov, G. P. Chernova, V. I. Kasarin, E. G. Mansky, T. A. Fedoseeva, V. V. Krasnoyarsky and T. P. Stepanova, Proceedings of the Third Conference on Titanium, Moscow State University, USSR (1976) 915-25.

[53] E. McCafferty and G. K. Hubler, *J. Electrochem. Soc.* **125** (1978) 1892-93.

[54] B. R. Appleton, E. J. Kelly, C. W. White, N. G. Thompson and B. D. Lichter, *Nuclear Instruments and Methods in Physics Research* **182** (1981) 991-99.