THE EFFECT OF PLATINUM GROUP METAL ADDITIONS ON THE CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF A 12% CHROMIUM FERRITIC STEEL

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DECLARATION

I, SIDNEY CHARLES DU PLESSSIS, declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not be submitted before for any degree or examination in any other University.

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Date

6/11/94

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SYNOPSIS

A comprehensive literature survey was undertaken covering the corrosion resistance of pgm alloying additions to austenitic, ferritic and duplex stainless steels. The effect of platinum, palladium and ruthenium additions to a ferritic stainless steel was investigated mainly from the point of view of corrosion resistance. The corrosion potential of 3CR12 alloy shifted in the noble direction when the pgm alloying additions were increased due to the polarization of the alloy by cathodic additions. The performance of 3CR12-0,2Ru alloy and 3CR12-0,25Pt alloy was better than the rest of the alloys in a reducing corrosive environment. The pitting resistance of these alloys was better than the rest of the alloys tested, including the base alloy 3CR12. In industrial woodpulp liquors, the 3CR12-0,2Ru and 3CR12 -0,25Pt alloys exhibited excellent corrosion resistance. The impact properties of 3CR12-Ru and 3CR12-Pd alloys were better than the 3CR12-Pt alloys.

CONTENTS

1. INTRODUCTION

South Africa is a major producer of platinum group metals, chromite and ferrochromium. Therefore it would seem appropriate to consider upgrading and expanding the market for these materials by developing and manufacturing Stainless Steels. A new ferritic corrosion resistance steel designated 3CR12 has been developed and patented by Middelburg Steel and Alloys. This 3CR12 corrosion resistant steel is intended to replace mild steel, galvanised steel and/or duplex coated steel in certain corrosion properties; it is expected to cut down the maintenance, repair and shutdown costs, i.e. be cost effective.

Because of the success achieved with Pd additions to Ti, it was decided to investigate the effect of platinum group metal additions on the corrosion resistance of a 12% chromium ferritic steel in various corrosive media. Platinum, palladium and ruthenium were added to a 3CR12 steel to a maximum of 0,5 weight percent. The scope of the work involved looking, at three series of alloys with different permutations of alloying additions and comparing their corrosion resistance established the optimum amounts of platinum group metal alloying additions at 0,2% ruthenium and 0,25% platinum.

2. LITERATURE SURVEY

2.1. THEORY AND MECHANISM OF PASSIVITY

The major theories for passivity, some of which were proposed initially by Schonbein and Faraday (1) and many other investigators such as Uhlig (2) who classified the theories into four main categories:-

(i) Metal Modification
(ii) Reaction Velocity
(iii) Oxide Film
(iv) Adsorption

Over the years consensus on any one theory has never been achieved. Of the various proposals, the oxide film and adsorption theories predominate in recent models of passive film formation; vestiges of all four theories are recognisable in some modifications of the adsorption theory.

2.1.1. Metal Modification Theories.

2.1.1.1. Valence theory of passivity.

Finklestein (3) suggested a metal modification viewpoint of passivity by considering passive iron to be made up of Fe^{3+}, and active iron mostly of Fe^{2+}. W.J. Muller (4) who modified this model, considered that polarization changed the electron density in the metal, and hence affect the relative proportions of ionic species in the metal with which electrons were in equilibrium.

2.1.1.2. Electron Configuration Theory.

Uhlig and Wulf (5) considered that there was the critical alloy composition above which, passivity is observed. However Tammann (6), earlier did some significant work on critical alloy compositions for passivity. The alloys of Cr-Fe were assumed to retain passive properties so long as the five d electron

vacancies per atom of Cr were filled by one electron per atom donated by alloyed Fe. This meant that passivity should be exhibited by alloys containing an atomic ratio Cr/Fe greater than 1/5 equal to 15.7 weight per cent Cr which is close to the observed 12 weight per cent Cr.

Uhlig (7) further expounded on his electron configuration theory by giving consideration to the type and structure of surface films that are formed on the metal or alloy surface. Uhlig suggested that an unfilled d electron configuration favoured a chemisorbed oxygen film whereas a filled d electron configuration favoured physical adsorption followed by a reaction to form an oxide film.

The solid solution alloys of the transition metals were suggested to be controlled by changes in the electron configuration which determined the composition at which an alloy changed its passive film characteristics from one of its components to that of another, e.g. alloys of Cr-Fe behave more like Cr above 12% and more like Fe below.

2.1.2. Reaction Velocity Theory

Max Le Blanc (8) proposed that the passive state is a result of the slow rate of metal dissolution independent of any surface film, e.g., hydrogen activation model.

Schmidt and Rathert (9) suggested that metals are usually in the passive state but become active in the presence of hydrogen. Forster (10) accepted hydrogen as a catalyst for accelerating the presumably slow anodic reaction whilst oxygen had the reverse effect. Smits and Atens (11) considered interstitial hydrogen to favour the active state by catalysing the formation rate of the lower valence species accompanied by rapid dissolution; however in the absence of hydrogen, the higher valence species is favoured accompanied by a slow reaction rate, viz., passivity.

2.1.3. Oxide Film theory

Faraday (12) may be regarded as the originator of the oxide film model of passivity. Various other researchers, such as Haber and Wetzlar (13) favoured Faraday's oxide film model.

Uhlig (14) suggested that the state of improved corrosion resistance was caused by the formation of a protective film on the metal surface consisting of the reaction products of the metal with the environment. This film is usually very thin and transparent and often consists of some kind of oxygen compound with the metal. Thus, when the passive state is established, the physicochemical properties of the metal relative to the corrosive medium depend on a large extent on the properties of the protective film (14,15).

2.1.4. Adsorption theory

The adsorption theory relies on the reduced reaction kinetics introduced by an adsorbed oxygen layer, or layers, on the metal surface. Tammann (16) applied the adsorption model to explain the passivity of chromium, stainless steels and similar metals. The adsorbed oxygen film was represented as satisfying surface metal affinities without dislodging metal atoms from their lattice, resulting in passivity.

In 1946 Uhlig (17) proposed that an adsorbed film is commonly the primary source of passivity. The adsorbed film derives support from the transition metals in accordance with their uncoupled d electrons interacting with oxygen to form a stable bond furthermore having higher energies of adsorption compared to non transition metals which would thus favour the retention of metal atoms in their lattice in preference to their removal to form an oxide lattice. The effect of the adsorbed film was to retard the dissolution reaction rate.

Cathodic polarization destroys passivity by both reducing the adsorbed oxygen film and evolving hydrogen on the metal surface which then contribute electrons to unfilled d electrons levels

and which compromise the ability of the metal to form a strong bond with adsorbed oxygen.

Halogen ions, such as the chloride ion breakdown passivity or prevent its formation in chromium, nickel, iron and stainless steel (18). The chloride ion adsorbs on the metal surface in competition with dissolved O_2 or OH^- resulting in an increase in exchange current density leading to the rate of metal dissolution being increased at a given potential.

As the more noble potentials are reached by anodic polarization of the metal, multilayer adsorption of oxygen builds up the passive film thickness. The adsorbed film eventually incorporates metal ions and protons in non-stoichiometric amounts (neutralizing negative charge) so that the aged passive film can be considered a non-stoichiometric oxide. Its eventual conversion to a stoichiometric oxide then places it in the diffusion barrier class; should it continue to offer some degree of corrosion protection it does so in the nature of the film hypothesized by the oxide film theory.

2.2 BREAKDOWN OF PASSIVITY AND REPASSIVATION

Z. Szklarska-Smialowska (19), Kolotyrkin (20) and more recently Kruger (21) have reviewed passivity breakdown. Pitting corrosion takes place in two stages:-

(i) nucleation or initiation of pits on the passivated metal surface, followed by

(ii) the propagation of the pits.

Pitting is an example of highly localised corrosion that appears on metal surfaces that otherwise show very low dissolution rates. Two opinions exist concerning the best methods for studying pitting corrosion (19). Some authors believe that pitting should be investigated by electrochemical techniques i.e. potentiostatic, potentiodynamic, or galvanostatic in which only the anodic reaction is considered. The alternative is to

consider both the cathodic and anodic processes simultaneously i.e. immersion tests in a chloride containing environment.

The tendency of a metal or alloy to pit can be estimated by:

(i) determination of the breakdown potential (22-30).

(ii) determination of the minimum concentration of chloride ions in solution causing pitting (31).

(iii) measurement of number and eventually, the depth and width in a suitable standard solution (32).

(iv) Critical pitting temperature, the temperature above which pitting has been observed to occur in oxidising acid chloride media and below which the metal or alloy is immune to the initiation of pits (26, 33, 34).

2.2.1. Theories of pitting

2.2.1 1. Ion-Migration Mechanism.

Hoar (35) assumed that the initiation of pits might be due to the adsorption of aggressive anions on the surface of the oxide film followed by the penetration of ions through the films. Anion entry, without exchange, into the film was postulated as producing a greatly induced ion conduction in the "contaminated" oxide film. The film becomes able at a certain point to sustain a high current density and to produce brightening by random removal of cations. When the field across the film solution reaches a critical value, pitting occurs.

Several studies have confirmed the contamination of the passive film by aggressive anions. By means of ellipsometric studies on pure iron, McBee, and Kruger (36) found that the addition of chloride ions to th solution produced changes in the properties of the oxide film which could be due to penetration of the film. McBee and Kruger (37) also found changes in the oxide films of Fe-Cr and Fe-Cr-Mo alloys which were exposed to chloride

media, but they were not as pronounced as iron. However Szklarska-Smialowska (38) showed with the aid of ESCA and Auger techniques that all the chloride was weakly bounded to the surface of the oxide film with no evidence of penetration.

2.2.1.2. Flaws and oxide film defects.

The mechanical breakdown process was formulated by Hoar who considered that during anion adsorption of water, molecules of the solution at the surface are replaced and this causes the lowering of the interfacial tension on the oxide-solution interface by the mutually repulsive forces between charged particles. The adsorbed anions push one another and the oxide to which they strongly adsorbed causing slip and forming cracks which are the nuclei of pits.

According to Sato (39) the electrostriction pressure produces a compressive stress which could exceed the breakdown stress of the oxide film. Wood et al (40) suggest that pitting starts at flaws present in the oxide film. Okamoto (41) carried out noise analysis of the passive film at constant potential either in the presence or absence of aggressive anions which suggests that in the passive film there is a dynamic balance between film breakdown and repassivation.

2.2.1.3. Competitive adsorption mechanism.

On the basis of the adsorption theory of passivation, Uhlig (14) described the formation of pits as a result of competitive adsorption of chloride ions and dissolved oxygen or hydroxyl ions. Breakdown of passivity by chloride ion occurs locally rather than generally over the passive surface at preferred sites being determined perhaps by small variations in the passive film. Pits develop on the spots where oxygen adsorbed onto the metal surface is displaced by Cl^- ions. According to this theory, the breakdown potential represents the minimum electrode potential value, at which the aggressive anions become capable of producing a reversible displacement of the passivating oxygen from the metal surface.

2.3. ELECTROCHEMICAL BEHAVIOUR OF ACTIVE-PASSIVE METALS.

From an electrochemical viewpoint, the phenomenon of passivity may be described by the schematic, anodic dissolution curve shown Figure 2.1.

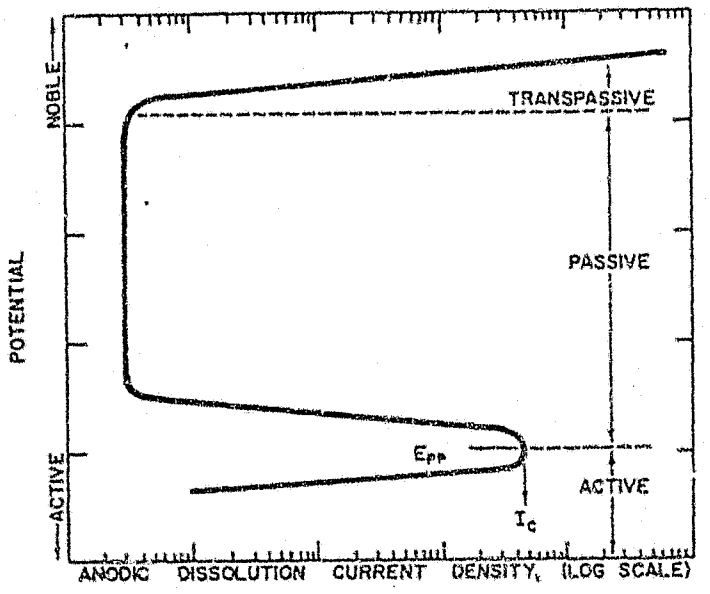

FIGURE 2.1:- Schematic anodic dissolution behaviour of a metal demonstrating an active-passive transition (42).

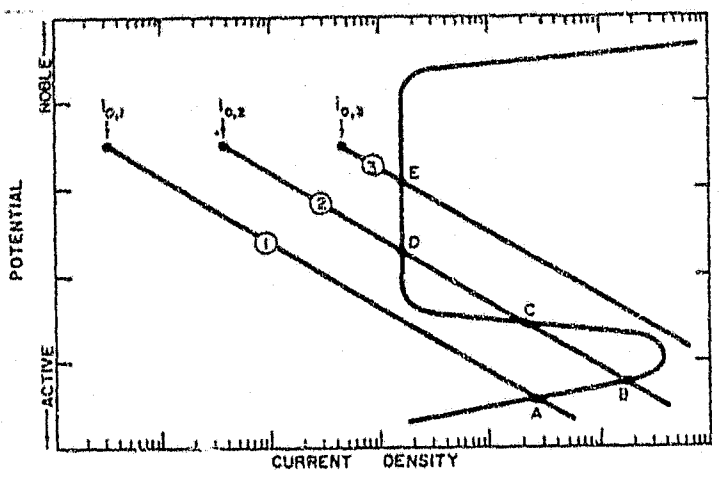

FIGURE 2.2:- Effect of cathodic exchange current density on the stability of the passive state (42).

When a metal is exposed to a corrosive media, two processes occur on its surface; oxidation and reduction. For a metal which demonstrates an active-passive transition, this can be illustrated by superimposing a cathodic reduction polarization curve. Figure 2.2 illustrates three different conditions which can arise when a cathodic process is superimposed (42). The three curves represent different activation control processes with different current densities. Considering case 1, the application of mixed potential theory indicates there is only one stable potential at A. In case 2 there are three points (B, C & D) where reduction rate equals oxidation rate; point C is electrically unstable. Hence, both points B and D are stable; B is in the active region corresponding to a high corrosion rate, while D is in the passive region with a low corrosion rate. There is only one stable potential E, in the passive region, for case 3. From a corrosion resistance viewpoint, case 3 is the most desirable and such a system will spontaneously passivate (43).

2.3.1. Degrees of passivity

The relative positions of the anodic and cathodic polarization curves in a passivation diagram (see Figure 2.2) graphically indicate the relative tendency of a metal or alloy to passivate in a given environment. Spontaneous passivation is possible only when the cathodic current ($i_{cat[Epp]}$) at the primary passive potential (Epp) is greater than the critical anodic current density for passivation (i_c). If alloying lowers i_c (perhaps by altering the adsorption process), then an active alloy may become passive if the above condition is achieved (44,45). Greene (42) has termed the ratio of these two important currents the "passivity index", P:

$$P = \frac{i_{cat[Epp]}}{i_c}$$

The magnitude of this passivity index is directly related to the degree of passivation of a system i.e. above a value of one corresponds to stable passivation while between zero and one describes the degrees of passivation of unstable and metastable passive states (44).

2.3.2. Passivity stabilization

Two basic methods are available to increase the stability of the protective film:-

2.3.2.1. Inhibition of the Anodic Process

Introducing alloying additions which directly facilitate passivity (for instance Cr, Si, Mo and/or Ni to an iron based alloy. Several metals (e.g. chromium) are naturally passive when exposed to most corrosive environments and they remain bright and tarnish-free over extended periods, in contrast to iron or copper which corrode or tarnish within a short time. It is found that the passive property of chromium is conferred to iron based alloys provided that 12% Cr or more is present. Iron-based alloys containing a minimum of 12% Cr are usually classified as the STAINLESS STEELS.

In the case of these alloys, the critical current density (i_c) and the critical potential (Epp) depend very greatly on the composition of the alloys. As an example, Figure 2.3 illustrates the position of the iron-chromium binary alloys in which the chromium content of the alloy is plotted against the critical potential for passivity in 0,1N H_2SO_4. An increase in the chromium content leads to the critical potential for passivity shifting towards negative values, which correspond to an increased ability of the alloy to become passive. However, this shift is irregular. An increase in the chromium content from 12 to 13 per cent is accompanied by an abrupt change in the potential to a value practically coinciding with the critical potential for passivation of pure chromium.

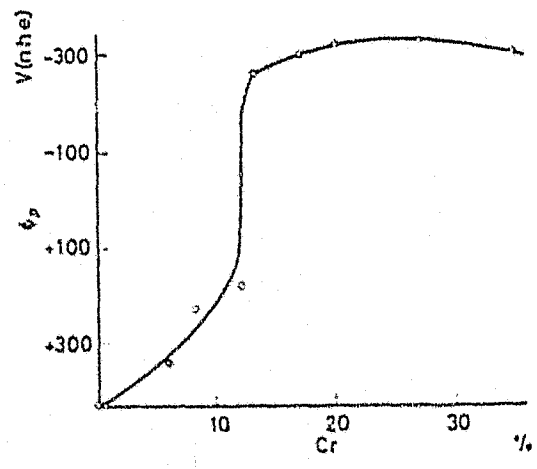

FIGURE 2.3:- Critical potential for passivity of Fe-Cr alloys as a function of the chromium content of the alloy in 0,1N H_2SO_4(46).

Figure 2.4 shows that, an increase in the chromium content is also accompanied by a pronounced decreased in critical current density for passivity.

An increase in the chromium content in binary alloys is not only accompanied by the above-noted changes of the critical current and potential for passivity; there is also a noticeable increase in the dissolution rate of the alloys in the region of potentials preceding passivity. That is why, despite the great ability of alloys with a high chromium content to become passive, in their active state they are also characterized by a lesser corrosion resistance. This is seen in Table 2.1 which gives the values of the corrosion potential and corrosion rates for a series of iron-chromium alloys in a sulphuric acid solution.

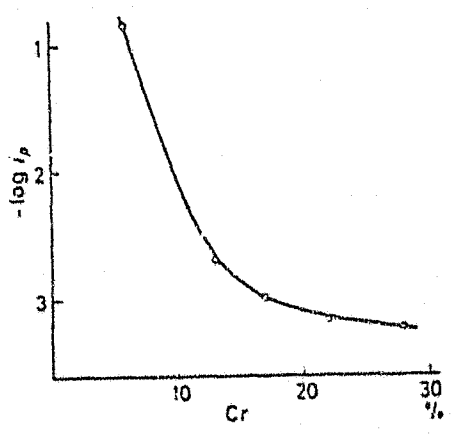

FIGURE 2.4:- Critical current density for passivity of Fe-Cr alloys as a function of chromium content of the alloy in 0,1N H_2SO_4 (46).

TABLE2.1

Corrosion potentials and rates of Fe-Cr alloys in de-aerated 1N H_2SO_4 at 20°C (46).

Chromium content (%)	*Corrosion parameters*	
	ϕ (Volts, Normal Calomel Electrode)	*i (A cm^{-2})*
0	−0·560	9×10^{-5}
0·1	−0·560	9×10^{-5}
4	−0·570	3×10^{-4}
8	−0·580	4×10^{-4}
12	−0·600	4×10^{-4}
20	−0·620	8×10^{-4}
27	−0·630	7×10^{-4}
35	−0·630	7×10^{-4}

On alloying iron with nickel, the passive properties of the alloys also increase, but to a lesser degree than alloying with chromium (47). The introduction of more than 8% Ni to chromium steels promotes a decrease in the critical current density (i_c), but shifts the primary passivation potential (Epp) in the positive direction (62). Alloying stainless steels with small amounts of elements such as Mo, Ni, V, Si, Ti and Nb (47,48) also improve passive properties of the alloy.

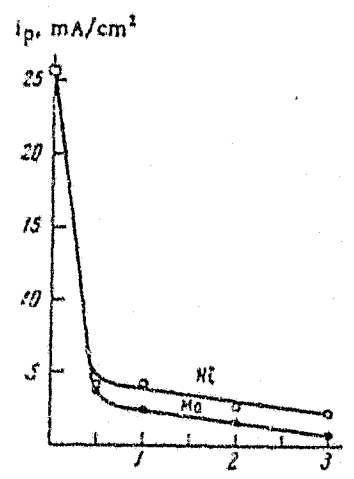

FIGURE 2.5:- Effect of Ni and Mo on the passivation of 25% Cr steels in 1 N H_2SO_4 at 25°C (47).

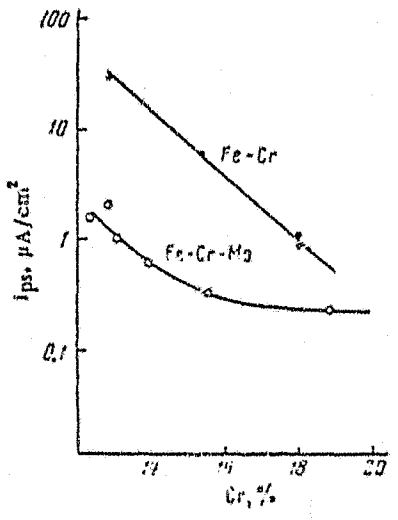

FIGURE 2.6:- Effect of an increasing chromium content in Fe-Cr and Fe-Cr-1%Mo alloys on change in the dissolution current density in the passive state (i_{ps}), 1 N H_2SO_4, 50°C (47).

Alloying chromium steels with nickel or molybdenum reduces i_c and increases the film stability in the passive region, but the passivation potential undergoes little change (48). It can be seen from Figure 2.5 that even as little as 0,5% of the alloying element lowers the passivation current 6-10 times.

Figure 2.6 shows the significant effect of molybdenum on change in the current density of the passive state. Alloying chromium steels of less than 20% chromium with 1% Mo reduces the magnitude of the passive current i_{pass} (or i_{ps}).

Tungsten has little effect on the passivation current and potential, but noticeably reduces the passive current density of an 18% Cr - 8% Ni steel containing 5-6% tungsten (49). Manganese in Fe-18% Cr steel has practically no effect on its passivity (42).

2.3.2.2. The noble metal alloying concept to obtain passivity.

According to what has already been discussed, passivity is obtained by producing a condition which results in a potential more noble than the critical potential for passivity. Without an externally applied potential, an alloy can attain a passive mixed potential only if the solution has a redox system with a reversible potential more noble than the critical potential for passivity of the metal (42, 45, 50). This is a necessary, but not sufficient condition for passivity (51).

Alloying can contribute to the passivation in two distinct ways:-

1. Alloy addition may affect those metal dissolution parameters (the critical anodic current and the critical anodic potential) which, in turn, determine the ease of passivation. This is the effect which Cr has on Fe in stainless steels. Increasing the Cr content decreases the critical anodic current (42) and moves the critical anodic potential in the active direction (52).

2. Alloy addition may influence the reduction kinetics of the cathodic process. Mixed potentials in the passive potential region are favoured by an increase in exchange current and a decrease in the cathodic Tafel slope (51).

Passivation by alteration of the cathodic process kinetics is of special interest when the critical anodic potential of the metal is more active than the reversible hydrogen potential of the solution (14,50). Under these circumstances, theoretically passivity can be achieved with the presence of a redox system no more oxidising than the hydrogen electrode. Under conditions where the metal exhibits a relatively high hydrogen overvoltage, a passive mixed potential may not be obtained directly. However, passivity can be accomplished by alloying such a metal

with an element which is essentially insoluble in the environment and which exhibits a high exchange current for the hydrogen ion reduction process (14,45). Slight corrosion will leave the alloy addition essentially in the elemental form on the surface. The surface can now function as bi-electrode, or galvanic couple, with one of the constituents presenting a low-hydrogen overvoltage surface. The exchange current for the hydrogen reduction on Ti is very small (53) resulting in an active mixed potential. When alloyed with noble metals e.g. Pt, Pd etc., regions with very high exchange currents are produced on the surface creating a mixed potential in the passive potential range. Under such circumstances, the alloy is described as 'self-passivating'.

2.4 THE MECHANISM OF THE EFFECT OF CATHODIC ALLOYING ELEMENTS.

2.4.1. Titanium-Noble Metal Alloys

An example of a self-passivating alloy developed through decreased i_c at Epp is Ti alloyed with 0,15% Pd. Stern and Wissenberg (50) showed that this approach led to the development of a corrosion resistant titanium alloy in hot hydrochloric and sulphuric acids. Theory predicts that anodic passivation of the titanium matrix will be achieved once sufficient noble metal has concentrated at the surface to provide the requisite galvanic exchange current to elevate the mixed potential of the system above a critical value (54). Corrosion tests in which coupons of titanium -0,15 per cent palladium are exposed to boiling 10 wt % sulphuric acid under stagnant and replenished conditions, provided an indication of the mechanism involved. In stagnant conditions there is an induction period of about 20 hours of rapid corrosion, followed by almost complete cessation of corrosion. If, however, the acid is replaced at daily intervals, successive increments in the amount of corrosion are recorded after each replenishment and there is no permanent passivity as shown in the graph of Figure 2.7.

Analysis of the acid at the onset of passivity shows that at this point the bulk liquor contains 0,9ppm of Pd. This suggests that initiallythe Ti_2Pd phase, as well as the matrix titanium suffers dissolution, and that when a sufficient concentration of palladium ions has built up in solution, metallic palladium is deposited on the metal surfaces (55). This could then bring into play the anodic passivation mechanism suggested by Stern and Bishop (56), and also Cotton (55).

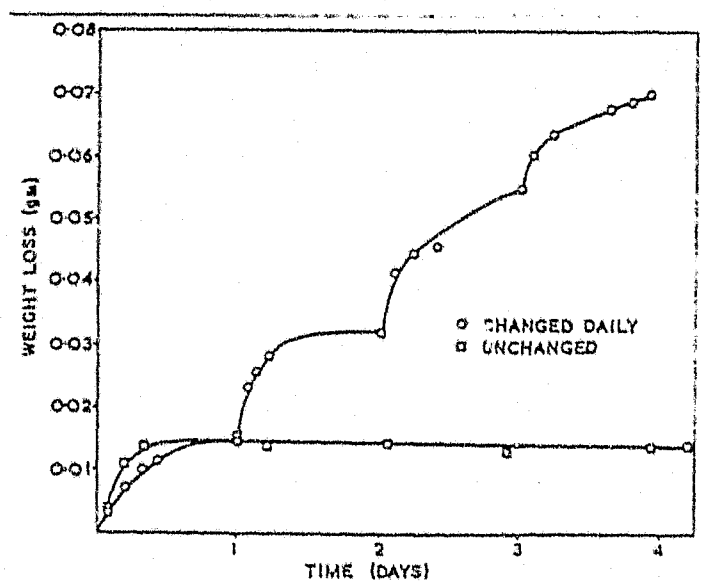

FIGURE 2.7:- Corrosion tests on Ti-0,15% Pd in boiling 10% H_2SO_4 (54).

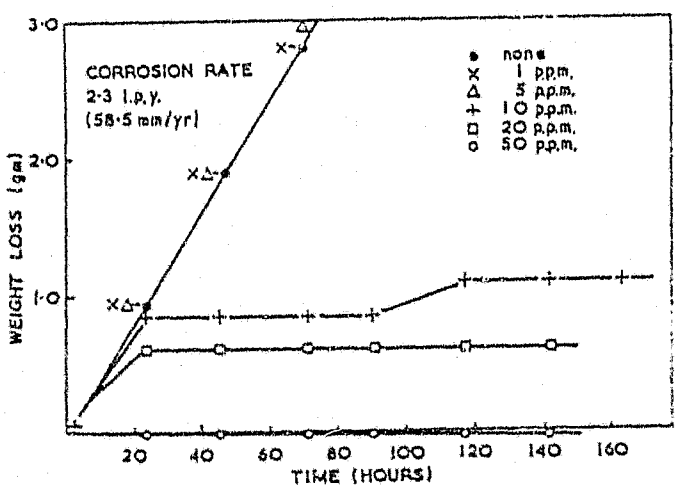

FIGURE 2.8:- Commercially pure titanum in boiling 10% H_2SO_4 with Pd additions. Solutions changed Daily (54).

These investigators consider that the surface becomes enriched in palladium and forms a galvanic couple between titanium and the metallic palladium. The induction period of rapid corrosion is necessary in order to build up the required soluble palladium. There is confirmation of this in that if the amount of alloying palladium in the alloy is increased from 0,15 to 0,5 per cent, the induction period virtually disappear, presumably because the requisite concentration of palladium build up more rapidly (57).

Further confirmation of this mechanism is (54, 58) obtained if unalloyed titanium is exposed to 10 weight per cent boiling sulphuric acid to which palladium chloride is added to provide incremental amounts of soluble palladium at levels from 1 to 50 ppm with the liquor being changed at regular intervals. Results illustrated graphically in Figure 2.8, show that the onset of passivity takes place when the concentration of soluble palladium reaches 10ppm. This is a considerably higher palladium level than that detected in the bulk liquor resulting from initial

dissolution of the Ti-Pd alloy, but this could be accounted for by the establishment of a concentration gradient in a thin layer of stagnant liquor at the surface of the alloy specimens.

At the 20 ppm soluble palladium level, there is visible evidence of the precipitation of metallic palladium at the titanium surface, but at a concentration of 50 ppm a dark oxide is formed, presumably containing some palladium. This is accompanied by a slow weight increase.

A protective film of titanium oxide could result from oxidation of soluble titanium followed by a precipitation process. Thus, when the titanium initially corrodes it passes into solution as Ti^{3+} and this will be oxidised by Pd^{2+} according to the reaction (54).

$$2\ Ti^{3+} + Pd^{2+} \rightarrow 2\ Ti^{4+} + Pd \downarrow$$

Ti^{4+} is unstable and precipitates as TiO_2.

This is a somewhat different concept of what is regarded as the normal anodic passivation of metallic titanium that is presumed to take place on the metal surface; it is probable that both mechanisms are involved in the build up of protective films on Ti-Pd (14,45).

Sedriks (59) carried out research on the Ti-Ru alloys. Ti-Pd alloys were also prepared so that a comparison could be made with corrosion rates calculated by Stern and Wissenberg (59) based on a 24 hour exposure. The corrosion rates of Ti-Ru alloys (59) and Ti-0,2 Wt% Pd alloy were evaluated by weight loss after four consecutive 24 hour exposures to fresh solutions (Figure 2.9 and Figure 2.10). Sedriks found that the performance of the Ti-Ru alloys compared favourably with the Ti-0,2 Wt% Pd alloy in boiling sulphuric acid.

In discussing dilute Ti-Pt alloys, Fontana and Greene (43) have retained the earlier concept of enrichment by preferential dissolution of Ti. The dilute Ti-Pt alloys are homogeneous

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In discussing dilute Ti-Pt alloys, Fontana and Greene (43) have retained the earlier concept of enrichment by preferential dissolution of Ti. The dilute Ti-Pt alloys are homogeneous

solid solutions, with the region of solid solubility of Pt in Ti extending to at least 1 wt %. Thus the point raised by Cotton (54) about intermetallics does not seem applicable to this system. However, there is some difficulty in finding an explanation for the process by which enrichment occurs in solid solutions as dilute as Ti-0,15 wt % Pd. In the solid solution with each noble metal atom surrounded by a large number of Ti atoms, it seems very likely that, as corrosion proceeds, the Pt atoms will find themselves detached from the solid simply by undermining and be released, brought about by the dissolution of the neighbouring Ti atoms (59). If this occurs, then the formation of the Pt enriched layer must also be considered as arising through a dissolution/re-precipitation mechanism.

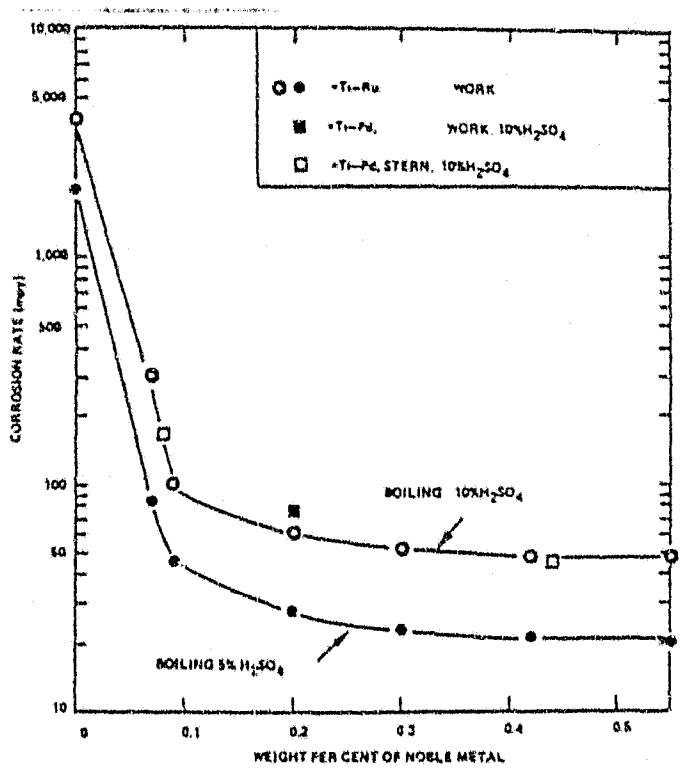

FIGURE 2.9:- Measured Corrosion rates of Titanium-Noble Metal alloys in boiling H_2SO_4 solutions (59).

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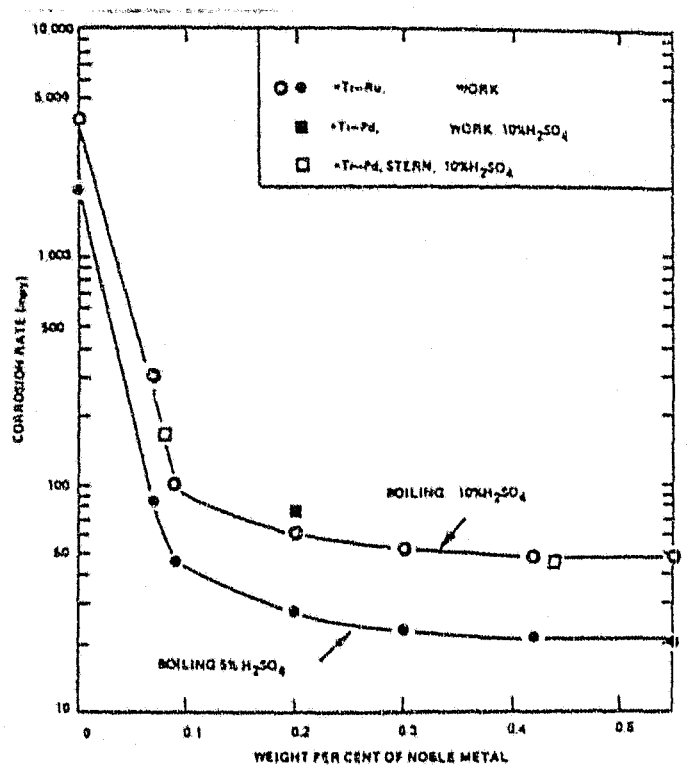


FIGURE 2.9:- Measured Corrosion rates of Titanium-Noble Metal alloys in boiling H_2SO_4 solutions (59).

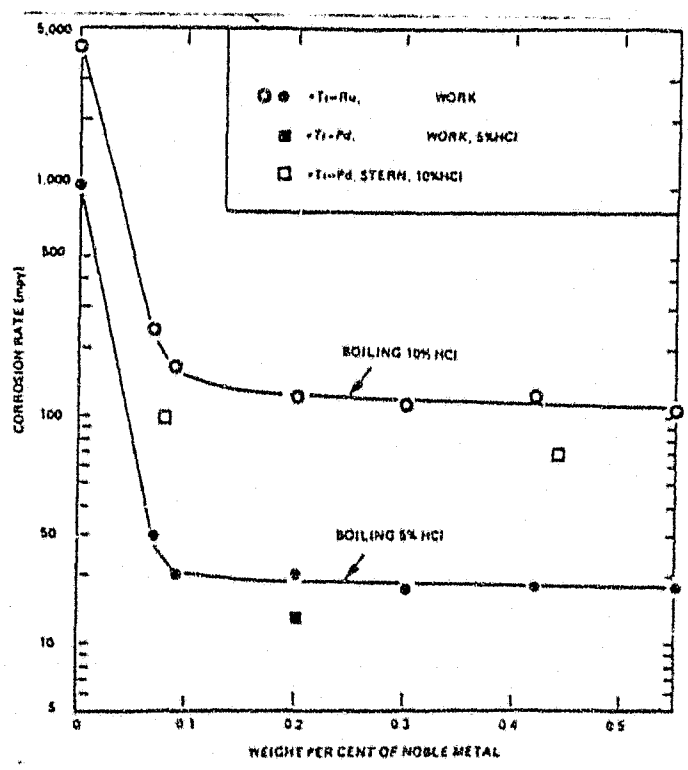


FIGURE 2.10:- Measured corrosion rates of Titanium-Noble Metal alloys boiling HCl solutions (59).

Buck and Leidheiser (60) compared the oxide ion size to the platinum group metal atoms and found that the atom with greatest mismatch, Pt, is only 4,5% greater in size than oxide ion. They proposed that the passivity imparted to the titanium by the platinum additions is a result of the stability given to the film by the platinum atoms in the substitutional positions.

Stern and Wissenberg (50) and Tomashov (61) carried out experiments on the general corrosion, and passivation of titanium alloys with small additions of noble metals in sulphuric and hydrochloric acid. Figure 2.9 and Figure 2.10. It is evident that maximum benefit to be derived from platinum metal additions is reached at quite small concentrations, (± 0,1 per cent) being somewhat smaller for hydrochloric acid than for sulphuric acid conditions.

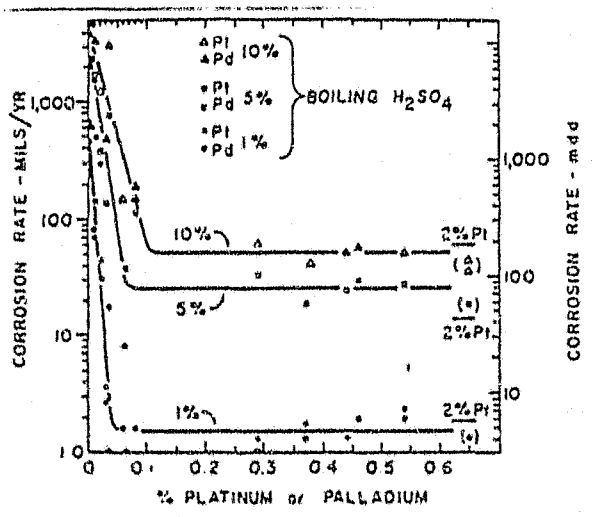


FIGURE 2.11:- Effect of Pt and Pd additions on corrosion rate of Ti in boiling H_2SO_4 (50).

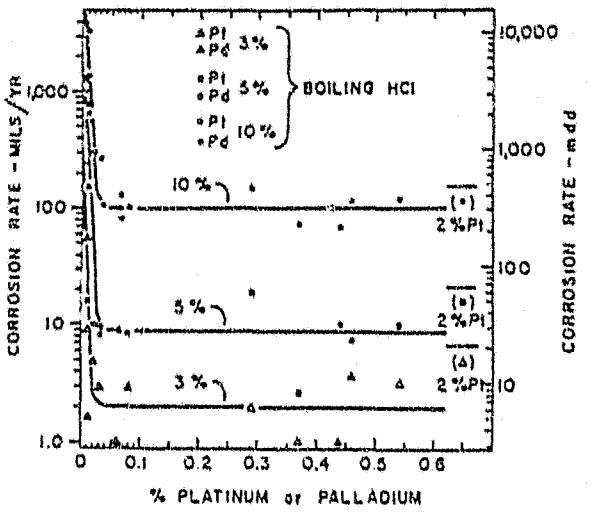


FIGURE 2.12:- Effect of Pt and Pd additions on corrosion rate of Ti in boiling HCl solutions (50).

Table 2.2 give some results. The small additions of all six platinum metals are seen to give marked improvements in corrosion resistance even in hot and fairly concentrated sulphuric and hydrochloric acid. Platinum, palladium, rhodium and ruthenium gave the best results; osmium and iridium appear to be slightly less effective. Similiar additions of rhenium, gold, silver and copper give either a small improvement, or an actual increase of corrosion rate, probably because they are less effective cathodes, with higher overpotentials (62).

TABLE 2.2

Effects of Various Alloy Additions on the Corrosion Resistance of Titanium

Composition	Weight Loss in 24 Hours (Mils/Year) Boiling H_2SO_4 1%	10%	Boiling HCl 3%	10%
Titanium	460	3,950	242	4,500
Ti + 0.064% Pt	< 2	145	< 2	128
Ti + 0.54% Pt	< 2	48	3	120
Ti + 0.08% Pd	< 2	166	3	100
Ti + 0.44% Pd	< 2	45	< 2	67
Ti + 0.1% Rh	< 2	26	5	96
Ti + 0.5% Rh	3	48	< 2	55
Ti + 0.1% Ru	3	187	5	280
Ti + 0.5% Ru	< 2	48	< 2	113
Ti + 0.11% Ir	< 2	359	3	120
Ti + 0.60% Ir	2	45	3	88
Ti + 0.10% Os	5	480	3	1,820
Ti + 0.48% Os	< 2	82	3	208
Ti + 0.11% Re	235	—	345	—
Ti + 0.36% Re	9	—	30	—
Ti + 0.11% Au	1,050	—	1,500	—
Ti + 0.48% Au	3	—	9	146
Ti + 0.04% Ag	500	—	334	—
Ti + 0.34% Ag	—	—	—	4,850
Ti + 0.17% Cu	470	—	340	—
Ti + 0.44% Cu	660	—	550	—

Figure 2.11 and Figure 2.12 are derived from 24-hour corrosion tests, and it is likely that active conditions at first prevailed in the alloys with lower noble metal contents, until sufficient amount noble metal became exposed to give the requisite amount of cathodic stimulation to produce passivation (50,62) (See Figure 2.13).

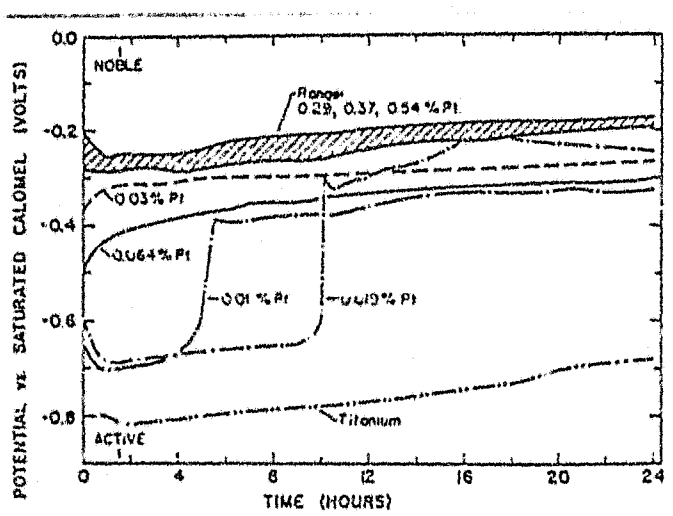


FIGURE 2.13:- Potential as a function of time for Ti alloyed with various concentrations of Pt in boiling 1% H_2SO_4 (59).

Alloying titanium with noble metals is not detrimental to behaviour in oxidising media, such as HNO_3 or ferric chloride. This is expected, since Ti does not exhibit a transpassive potential region where dissolution rate increases at quite noble potential values (50). The great improvement brought about by palladium alloying in non-oxidising media is illustrated by the results given in Table 2.3 for seven acid media.

TABLE 2.3

Comparison of the Corrosion Resistance of Titanium-Palladium Alloy with Commercially Pure Titanium in Various Non-Oxidising Type Media.

Environment	Corrosion Rate—Mils Year	
	Commercially Pure Titanium	Titanium-Palladium Alloy
Aluminium chloride, 10%, boiling	1	<1
Aluminium chloride, 25%, boiling	2020	1
Citric acid, 50%, boiling	17	<1
Formic acid, 50%, boiling	143	3
Hydrochloric acid, 5%, boiling	1120	7
Oxalic acid, 1%, boiling	1800	45
Phosphoric acid, 50%, aerated, 70 C	405	71
Phosphoric acid, 10%, boiling	439	127
Sulphuric acid, 5%, boiling	1920	20

Stern and Bishop (62) concluded that a titanium -0,2% palladium alloy is second only to tantalum as regards corrosion resistance in strongly acid media that are either oxidising, non oxidising or reducing, or which fluctuate in these respects. This alloy is superior to titanium in being as good in oxidising acids and much better in reducing acids.

2.4.2 Chromium-Noble Metal Alloys

A similar series of corrosion resistant alloys can be made up (see Table 2.4), based upon chromium (cf. Table 2.2), but these may not resist oxidising acids. The explanation for this difference lies in the anodic polarization curve for chromium (see Figure 2.15) which unlike titanium possess a transpassive region (56). Hence, noble metal alloy additions are detrimental to its corrosion resistance in highly oxidising media (50).

When chromium is alloyed with small amounts of platinum, palladium and other noble metals (63,64), its corrosion resistance to non-oxidising acid is markedly improved. Tomashov established two mechanisms for corrosion resistance of chromium alloyed with small additions of ruthenium in dilute sulphuric acid (65,66).

1. Blocking mechanism, in which atoms of ruthenium that are in solid solution, function as "stoppers" of the active sites of the crystal lattice, and directly reduce the rate of the anodic process of the alloy dissolution.

2. Screening mechanism, in which the finely dispersed powder of ruthenium, accumulating on the surface, and the molecular hydrogen filling the pores between the particles of ruthenium screen a part of the surface effectively operating as the anode.

Greene (63) verified that the dissolution of chromium leads to enrichment of the alloy surface in the noble element. The cathodic polarization curve of the alloy is gradually flattened until the critical current is exceeded and the alloy goes passive (45). In boiling 65% HNO_3 (63) the presence of alloying elements, especially platinum, gold and ruthenium, is detrimental to the corrosion resistance (Table 2.4). This is a direct consequence of the transpassive region exhibited by chromium. The corrosion potential of chromium in boiling 65% HNO_3 is very noble and is probably very close to the beginning of its transpassive region. Alloying with an inert element having a greater exchange current density for the reduction of HNO_3 than chromium shifts the mixed potential into transpassive region, where chromium dissolves as Cr^{6+} and the dissolution rate of the alloy is increased (45,63). This is illustrated schematically in Figure 2.14.

TABLE 2.4

Effect of Alloy Additions on the Corrosion Resistance of Chromium (63)

CORROSION RATE IN MILS/YEAR

Addition	Boiling H_2SO_4 10%	20%	30%	40%	50%	60%	90%	Conc.	Boiling HCl 5%	10%	15%	Boiling 65% HNO_3
Pure Cr	D(a)	D	D	D	D	D	2,400	300	D(b)	D	D	3
0.5% Ir	1	2	13 (49)	43	100	D	-	-	1	2 (20)	D	34
0.5% Rh	--	3	16 (23)	68	66	970	-		1 (11)	3 (45)	D	5
0.5% Ru	2	11	17 (48)	83	7,100	-	-	- -	1 (11)	1 (D)	D	100
0.5% Pt	3	12 (16)	28	175	120	36	D	185	1	8 (25)	D	200
0.5% Pd	2	8 (14)	22	180	1,500	1,300	- -		1 (56)	D	D	15
0.5% Os	1 (18)	67	560	-	-	--	-	- -	5 (2,800)	D	D	8
0.5% Au	600	1,900	- -	-		-	-	- -	D	-	-	120
0.5% Re	D	D	-			-	-	-	D	-	-	5
2% Cu	2,700	D	D	D	-	-	-	-	D	D	D	70
0.5% Ag	--		- -	---	---	--	---	-	D	-	--	4

D = Dissolved during test
( ) Samples activated with an iron wire for at least one minute
(a) Corrosion rate 100 000 mpy (0.5 hr. test)
(b) Corrosion rate = 240,000 mpy (0.5 hr. test)

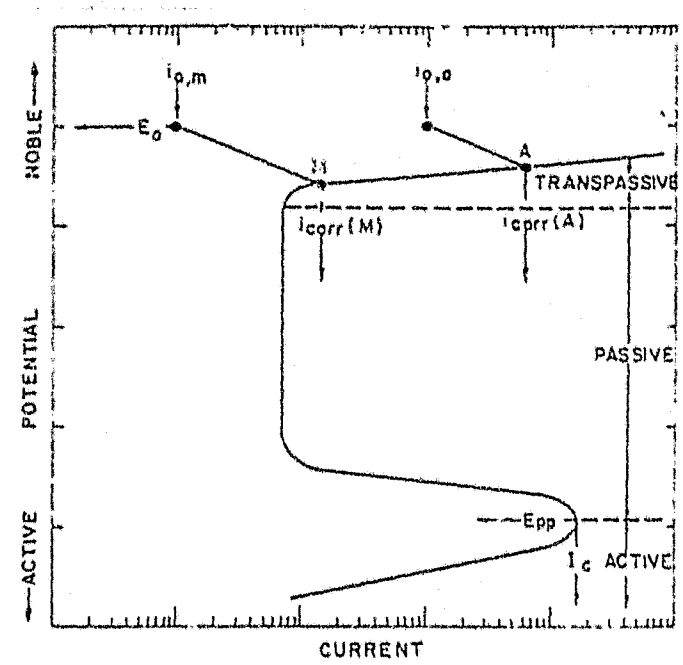


FIGURE 2.14:- Effect of Exchange Current Density on corrosion behaviour in transpassive region (Schematic) (63).

Under these conditions the anodic dissolution curve of a typical metal demonstrating active, passive and transpassive behaviour is shown. E_o is the redox potential of the medium, and $i_{o,m}$ and $i_{o,a}$ are the exchange current densities of the pure metal and a noble metal alloy, respectively. Provided that the alloying element is unattacked and has an exchange current density greater than the base metal, and that the mixed potential of the pure metal is close to the transpassive region, the corrosion rate is increased. The pure metal corrodes at potential M at a rate $i_{corr(M)}$ while the alloy corrodes at A with rate $i_{corr(A)}$.

TABLE 2.5

Effect of Platinum and Palladium Alloy Content on the Corrosion Resistance of Chromium (67).

CORROSION RATE IN MILS/YEAR

Addition	Boiling H_2SO_4 20%	30%	40%	50%	60%	70%	Boiling HCl 5%	10%	15%	Boiling 65% HNO_3
Pure Cr	D	D	D	D	D	D	D	D	D	3
0.1% Pt	5 (11)	22	100	840	D	D	< 1	9 (1,400)	D	9
0.5% Pt	12 (16)	28	175	120	36	D	< 1	8 (25)	D	200
1.0% Pt	6 (3)	22	210	68	21	1,260	< 1 (5)	140	D	500
2.0% Pt	6 (18)	18	120	28	9	56	< 1	3 (51)	D	300
5.0% Pt	1 (4)	18	51	12	-	55	< 1 (1)	170 (280)	D	490
0.05% Pd	0.22 (56)	57		D	D		D	D		6
0.1% Pd	0.20 (20)	31	130	1,600	D		0.04 (915)	D		5
0.2% Pd	0.13 (13)	23	150	1,400	D		0.36 (94)	D	-	7
0.3% Pd	1.12 (13)	21	370	1,400	300		1 (48)	D		5
0.5% Pd	8 (14)	22	180	1,500	1,300		1 (56)	D	D	15
1.0% Pd	2 (16)	56	2,800	725	400		2 (13)	D	D	23

D Dissolved during test
( ) Sample activated with an iron wire for at least one minute

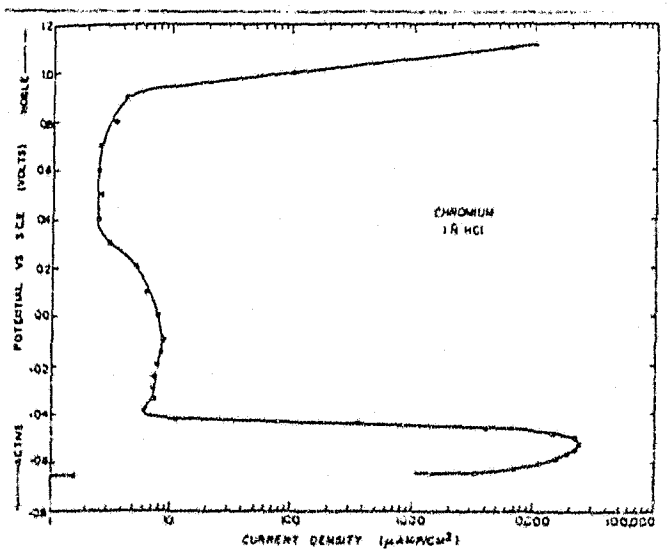


FIGURE 2.15:- Anodic Polarization of chromium in H_2 saturated HCl at room temperature (63).

TABLE 2.6

Critical anodic current densities (i_c) of Cr alloys in $1NH_2SO_4$ at room temperature, potential held at -0.600V for 3 hours (63).

Alloy	Calculated critical anodic current (i_c), ma/cm²	Applied cathodic current, ma/cm²: Initial, 5 min	Final, 3 hr
Cr + 0.5% Ir	0.055	132	136
Cr + 0.5% Pd	0.130	40	600
Cr + 0.5% Rh	0.145	600	900
Cr + 0.5% Pt	0.315	115	210
Cr + 0.5% Os	0.380	232	228
Cr + 0.5% Re	10.0	12	86
Cr + 0.5% Ag	12.5	10.4*	2.5*
Cr + 0.5% Au	15.8	20	230

* Anodic current.

Table 2.4 supports the above hypothesis. Small amounts of osmium, palladium, rhenium and silver which are rapidly attacked by HNO_3 have a negligible effect on the corrosion resistance of chromium in HNO_3 (63, 67). Due to their high corrosion rates, these elements cannot accumulate appreciably on an alloy surface. At high alloy contents detrimental effects are observed as shown by palladium in Table 2.5. This is probably

the reason for the poor HNO_3 resistance of chromium - 2% copper. Platinum, iridium, ruthenium, gold and rhodium are unattacked by hot, concentrated HNO_3 (67). All these elements with exception of rhodium, markedly reduce the corrosion resistance of chromium. The reason for rhodium exhibiting this behaviour is due to the fact that it is insoluble in nitric acid and accumulates on the chromium surface which would otherwise be a poor catalyst for the cathodic reduction of nitric acid (63).

Here it is shown that noble metal alloy additions can affect both anodic and cathodic reaction kinetics. A noble element simultaneously can increase cathodic exchange current density and decrease the critical anodic current density when alloyed with a metal. The corrosion resistance of a noble metal is quite likely related to the type and structure of the noble metal deposit on its surface. A loose, porous deposit would have high surface area and, consequently, a high apparent cathodic exchange current density. Such a deposit would have little effect on anodic dissolution rate. The chromium-gold alloy appears to be an example of this effect (63). Its hydrogen overvoltage is surprisingly low and its critical anodic current density value is similar to pure chromium. A smooth, dense surface deposit of noble metal should markedly affect anodic dissolution while demonstrating a relatively high hydrogen overvoltage. The behaviour of chromium-iridium is consistent with this model (See Table 2.6 and Figure 2.15).

2.4.3. Stainless Steel containing noble metal additions

Tomashov and his colleagues were the first to demonstrate the possibility of considerably enhancing the passivation of 18-8 type stainless steel in aqueous sulphuric acid by the additions of small amounts of platinum and palladium (52, 68, 69).

If the surface of stainless steel is made much more catalytically active for the cathodic reduction of oxygen or, still better, of hydrogen ion, larger current densities at more positive potentials could be obtained at any anodic zones.

2.4.3.1. Austenitic 18Cr-8Ni Stainless Steel

Tomashov and Chernova (69) prepared stainless steels containing small additions of noble metals designed to provide especially active cathodic zones for such reactions. Using as a base composition on austenitic chromium-nickel steel containing 18 per cent Cr and 9 per cent Ni (52, 69), they added 0,1 per cent platinum, 0,1 per cent palladium, 0,9 per cent palladium and 1,2 per cent copper. They exposed the four new alloys and the control alloy to 20 - 40% sulphuric acid, for 360 hours at 20°C and determined the corrosion resistance (or completeness of passivation) by the steady rate of hydrogen evolution (after passivation had set in). It may be seen in Figure 2.16 that the alloying additions were increasingly effective in the order, Cu → Pd → Pt. Also an increase in palladium content from 0,1 to 0,9 per cent increased the effectiveness. It was found that 0,1 per cent of platinum was at least as effective as 0,9 per cent of palladium, except at the highest acid concentration.

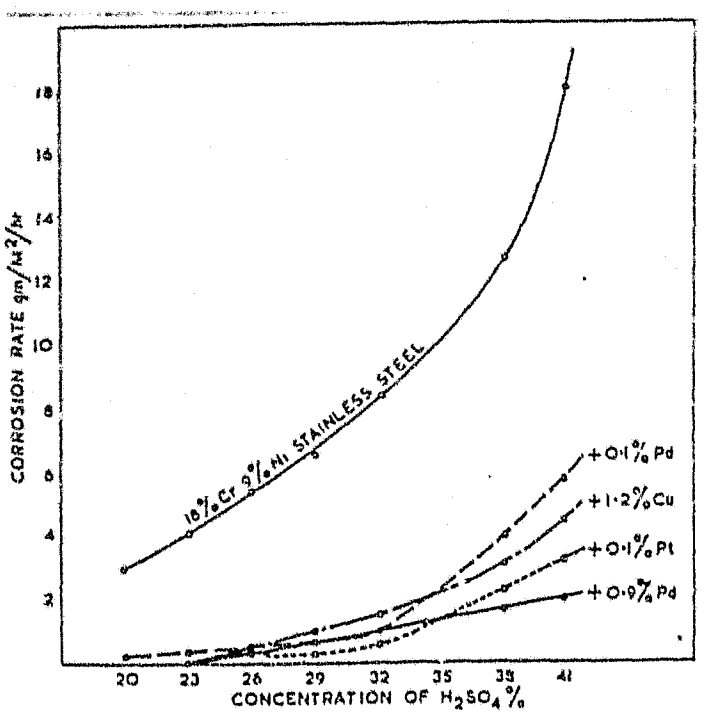


FIGURE 2.16:- Rate of corrosion of Cr-Ni stainless steels alloyed with Pt, Pd and Cu, in relation to concentration of H_2SO_4 (69).

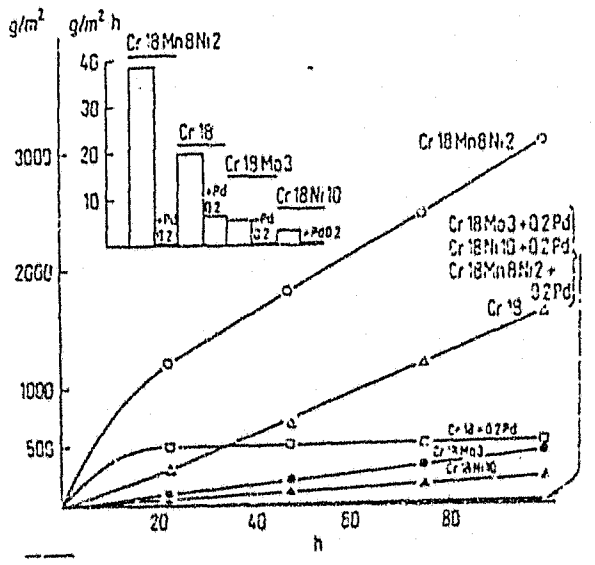


FIGURE 2.17:- Results of the effect of Pd additions on corrosion resistance of stainless steel (18%Cr) in 20% H_2SO_4 at 20°C (70).

Tomashov investigated the self passivation process and corrosion resistance of Fe-18Cr - 0,2 Pd alloys (70) containing various alloying elements in 20% sulphuric acid (see Figure 2.17). The addition of Pd to Fe-18Cr alloys causes self-passivation and considerably enhances corrosion resistance. The self-passivation of the alloys with Pd (70,71), which results from the accumulation of Pd on the surface during the initial period of an active dissolution and potential shift to the positive range (analogous to Ti-Pd passivation mechanism), depends on the possibility of passivation of the base alloy under the conditions present, during this stage shifting of alloy potential occurs.

Besides introducing cathodic elements into the alloy, it also is beneficial to increase the passivity of the anodic background (52), by using a basically passive alloy, such as titanium. For chromium - nickel steels containing 18 per cent Cr and 8 per cent Ni in solid solution this process of passivation, as demonstrated, goes on much easier. It may be assumed that further addition of chromium to the solid solution will further facilitate passivation at the expense of the newly included cathodic structural constituents.

The possibility of increasing the corrosion resistance of stainless steels used in nuclear reactors by alloying them with platinum has been considered by Chaudron and Griess (72,73). Griess (52) carried out tests at 250°C in heavy water solution of uranyl sulphate and copper sulphate have shown that introduction of 0,5% Pt into Type 304 stainless steel reduces the corrosion rate from 0,89 to 0,38mm/year. On increasing the rate of liquid flow, no substantial improvement in corrosion resistance was contributed by cathodic alloying component. However, in solutions containing uranyl nitrate and copper nitrate, the corrosion resistance was increased for both low and high rates of liquid flow. Further corrosion tests on the 0,5 per cent platinum alloyed 304 stainless steel were to be undertaken in view of its possible application in homogeneous reactors in which uranyl sulphate and nitrate solutions may be used as fuels (52,72).

2.4.3.2 Ferritic 18Cr Stainless Steel

Biefer (74) carried out a systematic comparison of the effect of alloying additions upon the corrosion resistance of Type 430 stainless steel, with the long-term objective of developing new stainless steel types have improved corrosion resistance.

The alloying additions selected were Mo, V, W, Ta, Si, Pd and Ge. With the exception of tantalum, these additions have good to high stability in ferritic stainless steel and the pure metals show good to excellent corrosion resistance in sulphuric acid.

A typical anodic polarization curve for AISI Type 430 Stainless Steel in normal sulphuric acid is presented in Figure 2.18. In Figure 2.19, which is a model anodic polarization curve of a type used by Tomashov (52), the effects of alloying additions are presented in qualitative form. The following effects of the additions would be expected to increase the tendency to passivate:

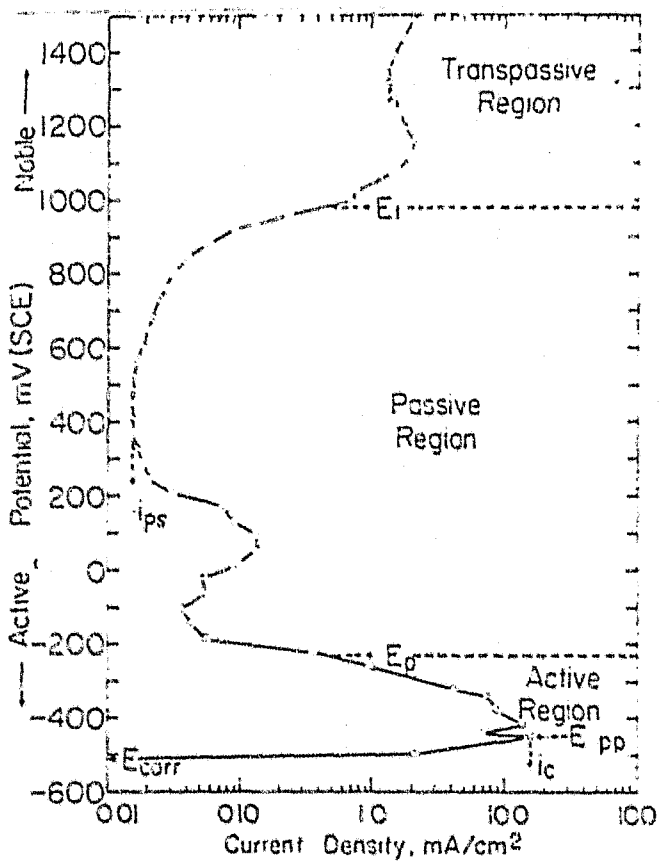


FIGURE 2.18:- Anodic Polarization Curve of AISI type 430 Stainless Steel in nitrogenated 1N H_2SO_4 (74).

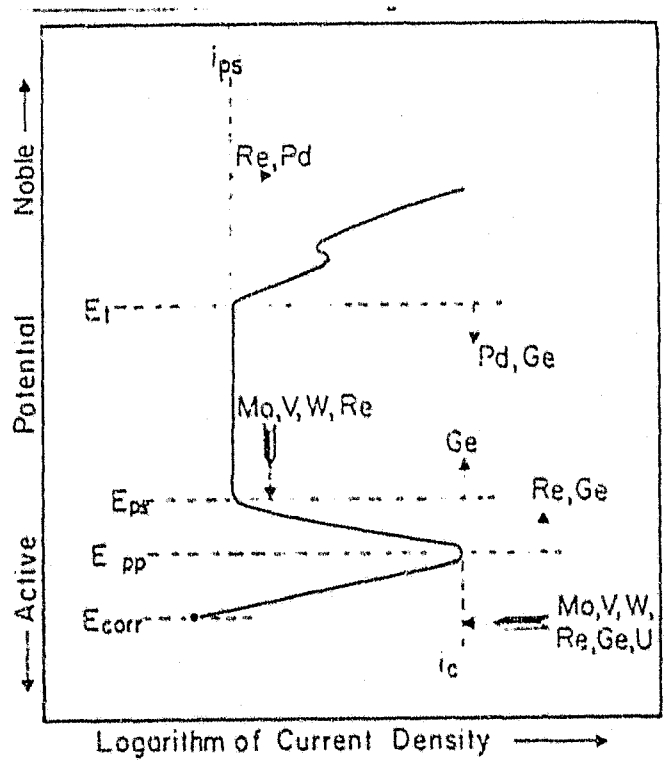


FIGURE 2.19:- Major effects of alloying additions on anodic polarization parameters in normal H_2SO_4 as shown qualitatively on a model curve. Decorated shafts show effects which increase the passivating tendency. (74).

1. Mo, V, W, Re, Ge and U bring about reductions in i_c.

2. Mo, V, W and Re bring about decreased (more active) values of E_{ps}.

Because the alloys containing higher palladium contents passivated spontaneously, part of the anodic curve was obscured. Hence, the effect of palladium upon Epp and i_c could not be determined directly.

In Figure 2.20 is presented the anodic polarization curve for 430 Stainless Steel to show the effect of alloying additions in normal sulphuric acid + 0,5 normal sodium chloride.

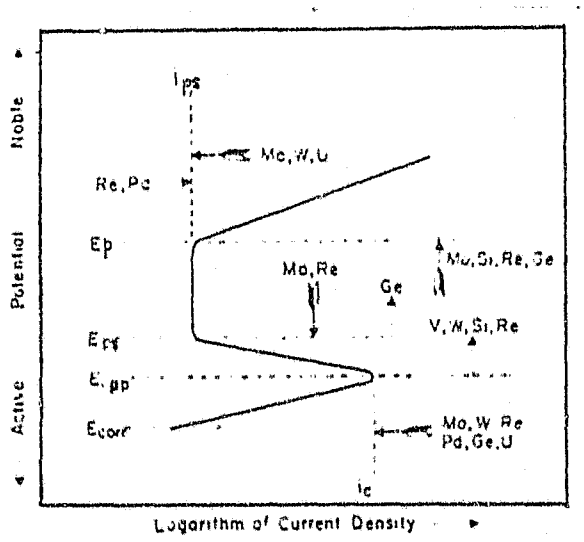


FIGURE 2.20:- Major effects of alloying additions on anodic polarization parameters in normal H_2SO_4 containing 0,5 normal NaCl as shown qualitatively on a model curve. Decorated shafts show favourable effects (74).

The two additions showing the strongest beneficial influence on corrosion behaviour were molybdenum and palladium. Molybdenum produced the most consistently favourable changes in anodic polarization behaviour, though it did not affect cathodic behaviour. The lowering of i_c values was insufficient to bring about passivation (74), but did produce lower corrosion rates in the active region in the weight-loss corrosion tests in normal solutions of sulphuric and hydrochloric acid.

Steels containing 0,46 per cent palladium or more, passivated spontaneously in nitrogenated normal sulphuric acid, showing potentials 500 to 600 millivolts more noble than the reversible potential for hydrogen reduction E_{rev}. These strongly positive potentials indicated that oxygen had not been entirely excluded from the solution but according to Greene (75), the presence of oxygen in sulphuric acid should not measurably effect the dissolution kinetics of Type 430 Stainless Steel. The action of palladium in bringing about passivation in normal sulphuric acid appeared to be due to its marked effect upon cathodic behaviour, as shown schematically in Figure 2.21.

In the tests in which specimen potentials were measured in sulphuric acid, standard Types 304 and 430 stainless steel showed little or no tendency to passivate Figure 2.22. In contrast, the alloy containing 0,99 per cent palladium showed reasonably extensive regions of spontaneous passivation at both high and low concentration levels and at temperatures up to boiling point. The region of very low corrosion are probably larger than shown in Figure 2.23, as consideration of the E_{ps} values shows that passivation could have occurred at negative potentials on the SCE scale (74).

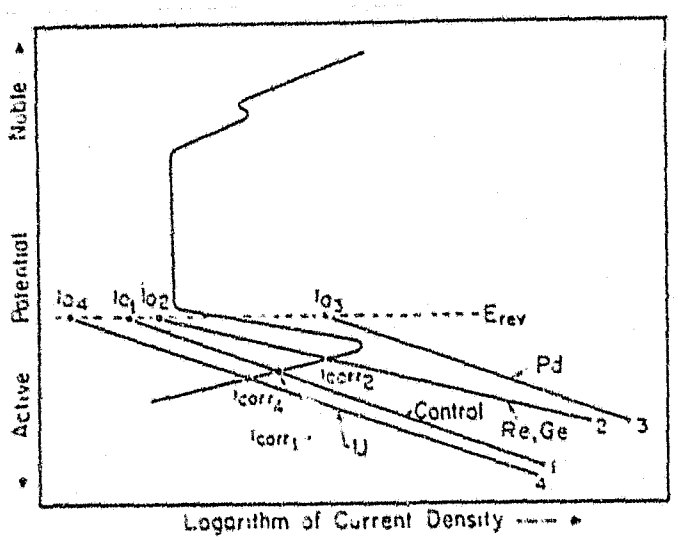


FIGURE 2.21:- Major effects of alloying additions on cathodic polarization behaviour in normal H_2SO_4 as shown qualitatively by model curves (74).

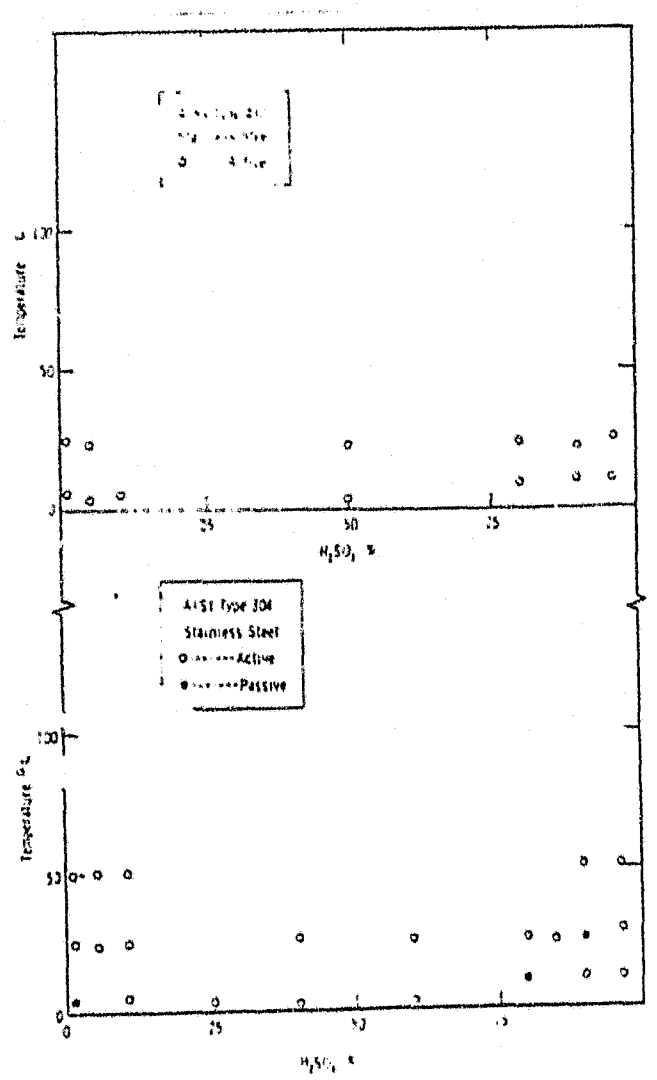


FIGURE 2.22:- Active-passive behaviour of AISI Types 430 and 304 stainless steel in H_2SO_4 (74).

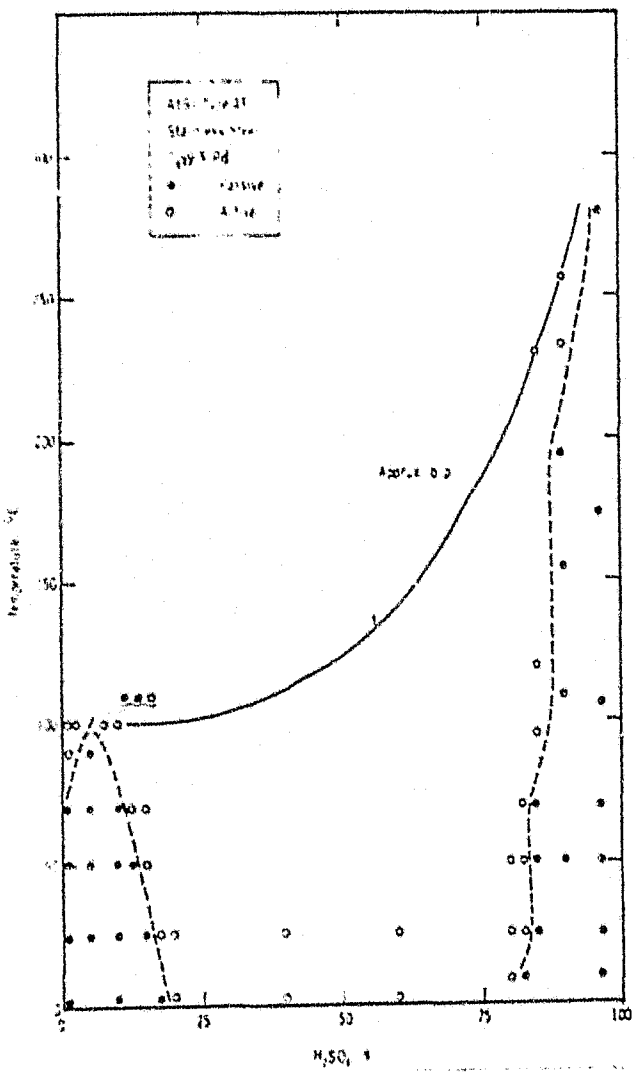


FIGURE 2.23:- Active-passive behaviour of Type 430 stainless steel alloyed with 0,99% Pd in H_2SO_4 (74).

The literature contains a great deal of information on the corrosion resistance in sulphuric acid of highly alloyed austenitic stainless steels. However, comparisons between this data and that for the Type 430 stainless steel containing 0,99 per cent palladium are difficult, because of widely differing experimental procedures and differing criteria for passivation. An added complication is that behaviour of the austenitics is highly dependent on the oxygen content of the sulphuric acid, corrosion rates being much lower in aerated than in air-free solution (76). However, in many cases, researchers do not supply details concerning the extent of aeration. The alloy containing 0,99 per cent palladium appears to be superior to even the most highly alloyed austenitics in concentrated sulphuric acid at high temperatures (77).

0,26 per cent Pd was insufficient to bring about passivity in normal sulphuric acid (74) (cf. passivation which was reported by Tomashov to be achieved in 20 per cent sulphuric acid by an addition of only 0,2 per cent Pd to 18 per cent Cr steel (70).) The necessity for higher palladium levels in Biefer's work was probably due to the use of Type 430 stainless steel base, with relatively high carbon and impurity content. Lizlovs and Bond (78) have shown, in anodic polarization measurements, that 17 per cent Cr steel based on high-purity materials outperforms a standard Type 430 stainless steel.

In the polarization measurements in a chloride-containing solution; palladium caused large increases in i_o and some decrease in i_c but this was insufficent to produce spontaneous passivation. Rather, increased corrosion rates in the active region were observed (Figure 2.24).

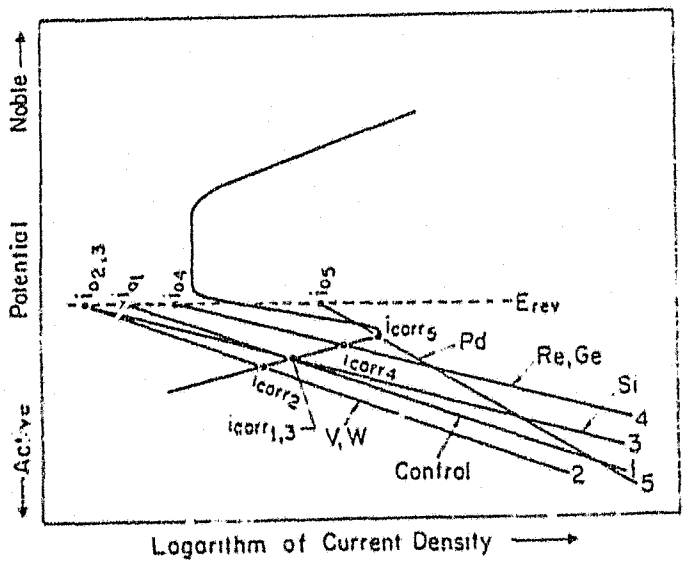


FIGURE 2.24:- Major effects of alloying additions on cathodic polarization behaviour in normal H_2SO_4 containing 0,5 normal NaCl, as shown qualitatively by model curves (74).

Corrosion rates were also high for the palladium-bearing alloys in the weight loss tests in normal hydrochloric acid and ferric chloride solutions. As noted, molybdenum has a strongly favourable influence on most anodic parameters in the presence of chloride.

Agarwala and Biefer (79) examined whether or not the additions affecting anodic polarization behaviour (Mo,V, W) could be combined synergistically with additions primarily affecting cathodic polarization behaviour (Pd, Ge, Re), to produce Type 430 stainless steels having markedly improved corrosion behaviour (Figure 2.25-2.28). Pd bearing alloys, such as 2% Mo-1%Pd, 2%V - 1% Pd and 2% W - 1% Pd passivated readily in 1N H_2SO_4 containing 0,5N NaCl, whereas Biefer showed (74) when each of four additions concerned acted individually, passivity was not achieved.

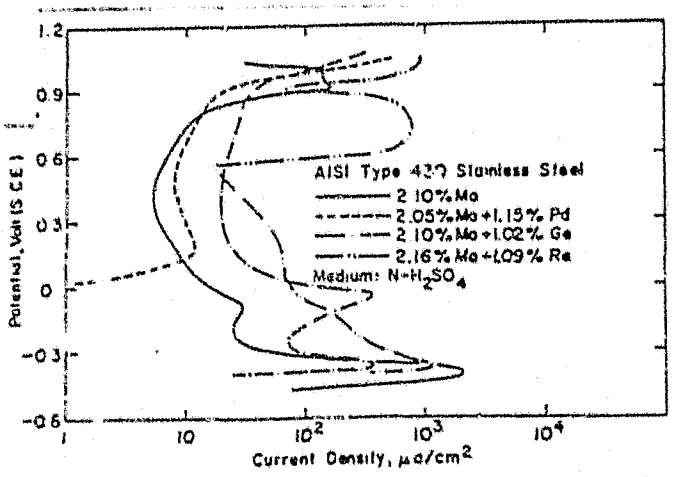


FIGURE 2.25:- Anodic polarization scans in nitrogenated 1N H_2SO_4 at 24°C (75°F) (79).

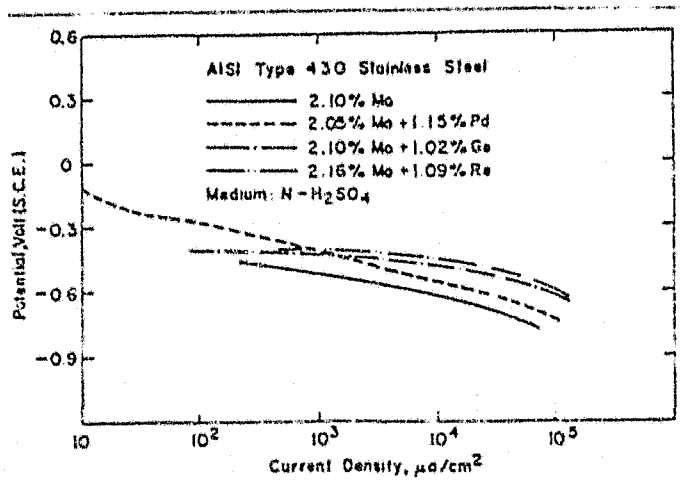


FIGURE 2.26:- Cathodic polarization scans in nitrogenated 1N H_2SO_4 24°C (75°F)(79).

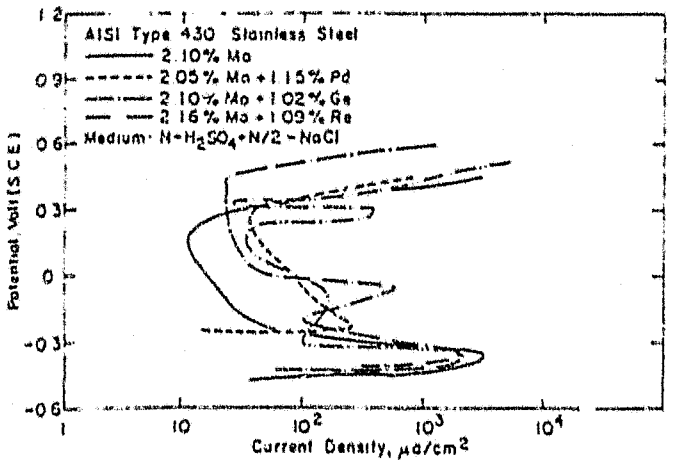


FIGURE 2.27:- Anodic polarization scans in nitrogenated in 1N H_2SO_4, 0,5N NaCl added, at 24°C (75°F) (79).

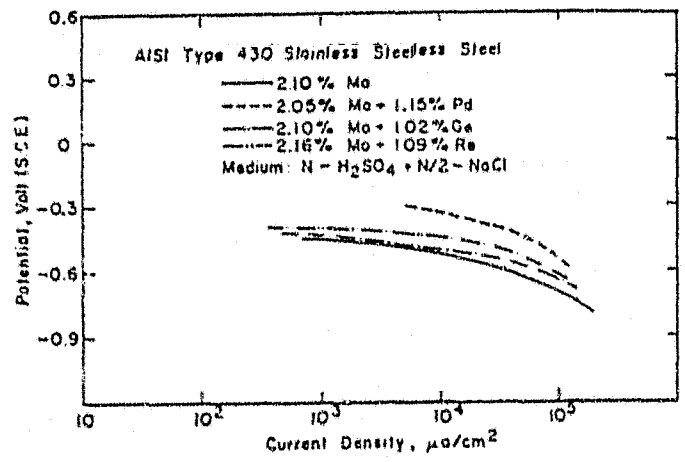


FIGURE 2.28:- Cathodic polarization scans in nitrogenated 1N H_2SO_4, 0,5N NaCl added, at 24°C (75°F) (79).

The results obtained on the Mo-Pd steel containing nominal levels of 2% Mo and 3% Mo showed that the presence of Mo enabled passivation in dilute sulphuric acid to be achieved at lower alloy contents than those repeated by Biefer (74). In the 3% Mo-Pd alloys, 0,19% Pd brought about borderline passivation in 1N H_2SO_4, while 0,48% Pd (though not 0,19% Pd) brought about passivation in 1N H_2SO_4 which contained 0,5N NaCl. In Type 430 steels with still higher Mo contents, further reductions of Pd, with retention of passivability, might be possible. It should be noted, however that Mo, while beneficial at dilute sulphuric acid concentrations, may be detrimental at high acid concentrations (Figures 2.23, 2.29-2.32). The regions of low corrosion rate in H_2SO_4 are probably more extensive than regions in which positive potentials were observed. (74).

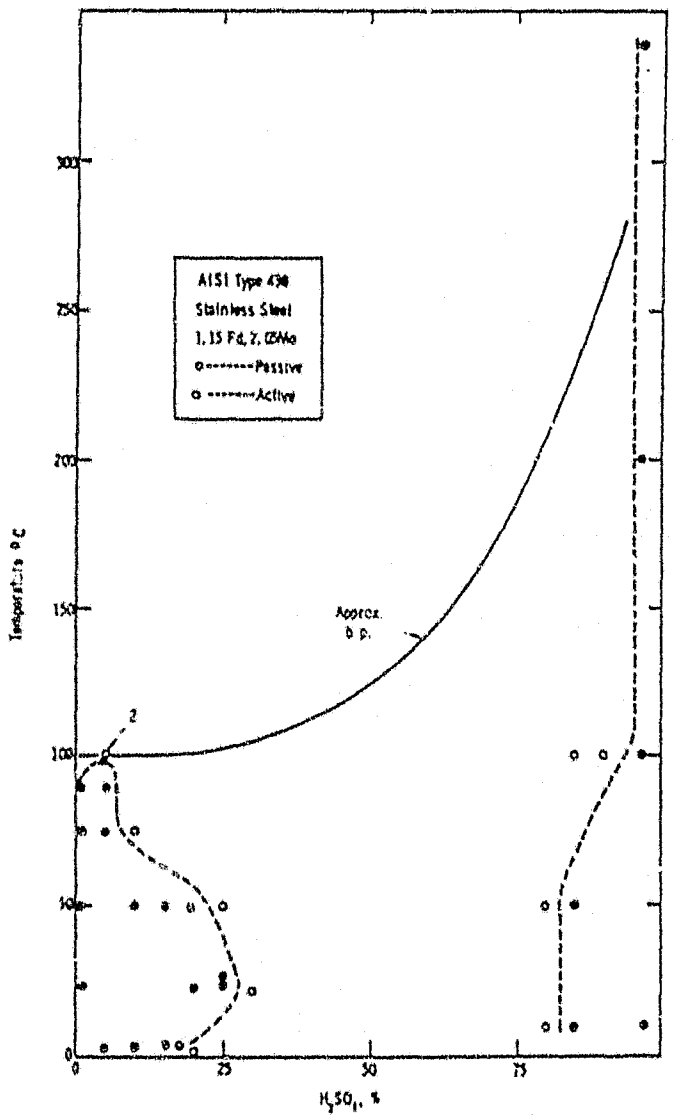


FIGURE 2.29:- Behaviour in stagnant H_2SO_4 of steel with nominal 2% Mo-1% Pd addition (79).

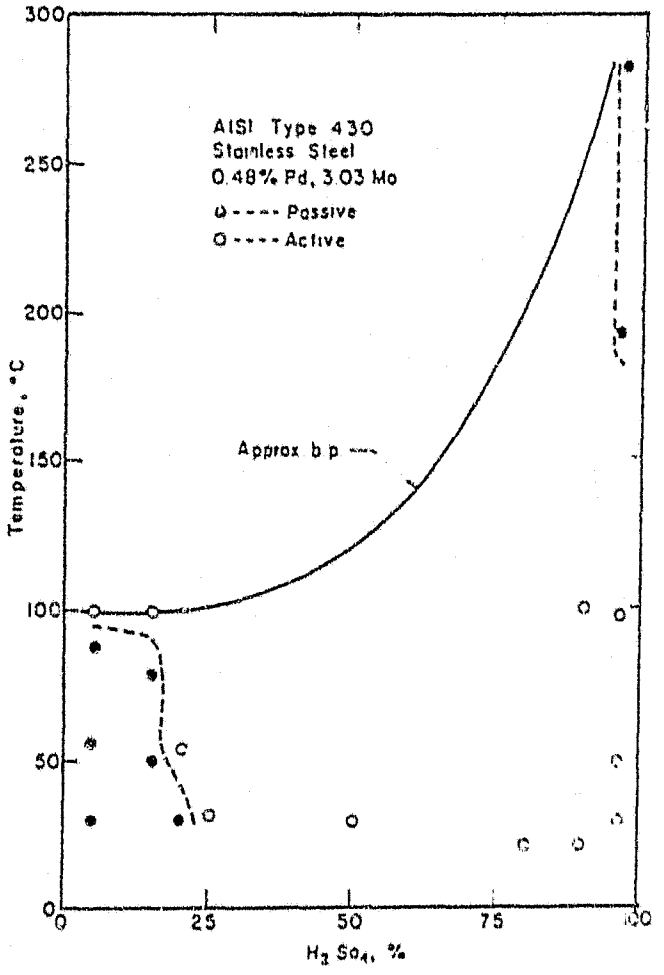


FIGURE 2.30:- Behaviour in stagnant H_2SO_4 of steel with nominal 3% Mo-0,5% Pd addition (79).

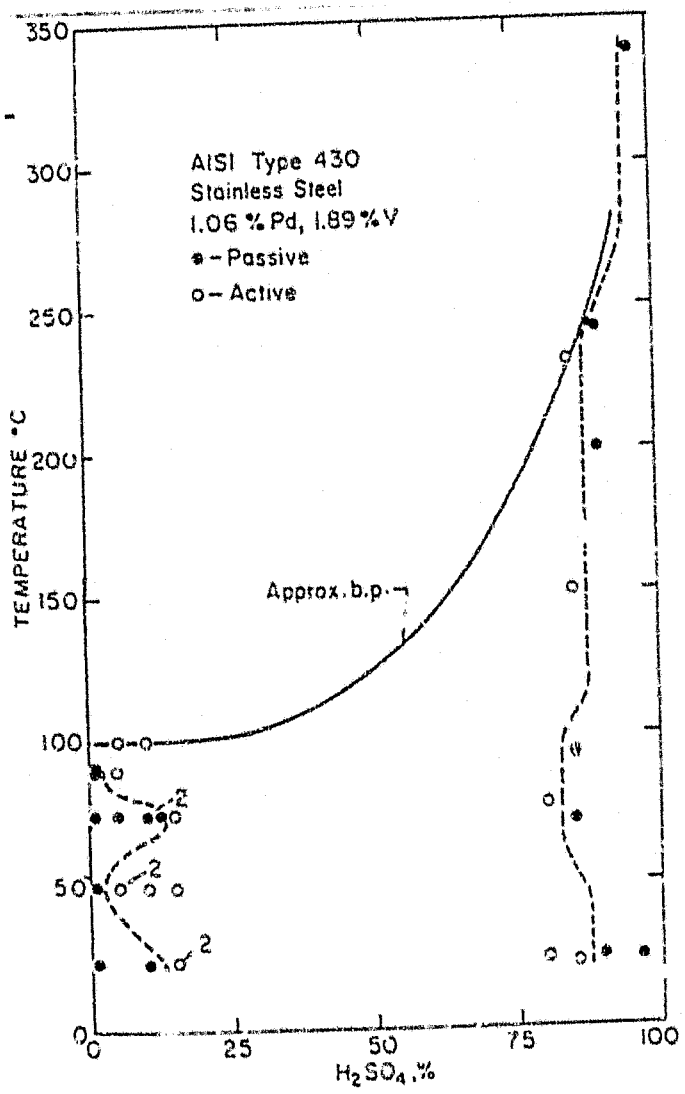


FIGURE 2.31:- Behaviour in stagnant H_2SO_4 of steel with nominal 2% V-1% Pd addition (79).

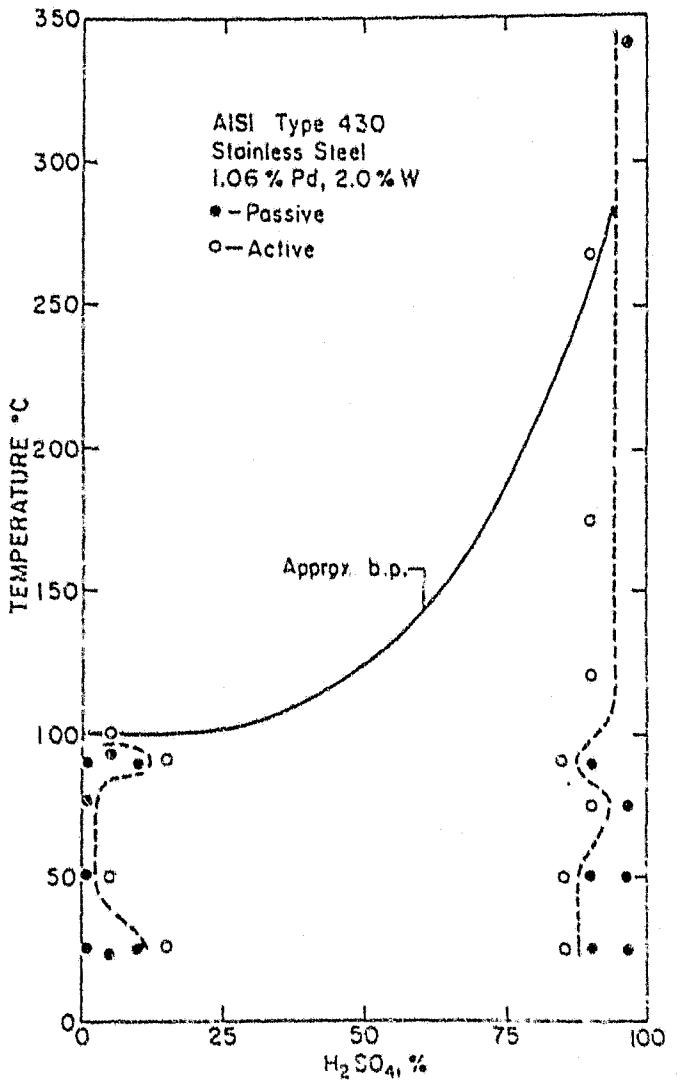


FIGURE 2.32:- Behaviour in stagnant H_2SO_4 of steel with nominal 2% W-1% Pd addition (79).

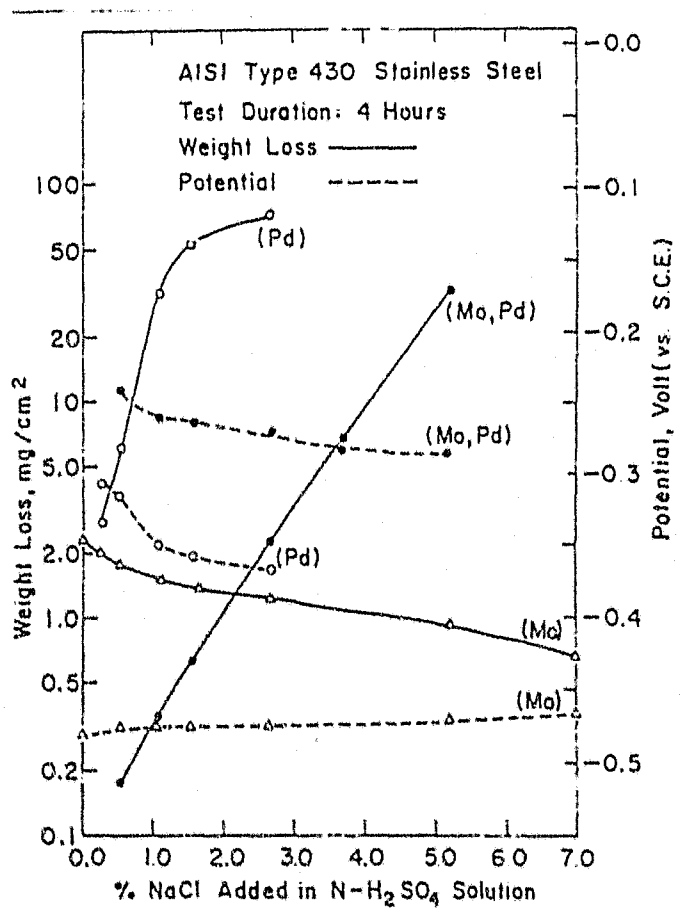


FIGURE 2.33:- Effects of NaCl additions to nitrogenated 1N H_2SO_4 at 24°C (75°F) on corrosion of steels containing Mo, Pd and Mo-Pd additions (79).

In 1N H_2SO_4 some of the Mo-Pd alloys can retain passivity in the presence of 2% to 3% NaCl. This contrasts with the results obtained for alloys containing Pd only, which showed extremely high corrosion rates under the same conditions (see Figure 2.29). A sufficiently high chloride concentration can still cause rapid corrosion of even Mo-Pd alloys.

The results of Table 2.7, shows that Type 430 stainless steel can be made passive in 1N H_2SO_4 by a prior surface deposition of Pd, support statements that Pd acts by means of a surface enrichment during an initial corrosion period.

TABLE 2.7

Effect of Pd Deposition on Passivation Properties of Type 430 Stainless Steel in Measurements at 24°C (75°F) (79).

	Period of Immersion in Stagnant $PdCl_2$ Solution						
	10 sec.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min. or more
Potential of unalloyed T-430 steel at end of each immersion	+256 mV	+185 mV	+181 mV	+177 mV	+189 mV	+168 mV	+155 mV
Potential of T-430 steel containing 2% Mo at end of each immersion	+360 mV	+228 mV	+228 mV	+234 mV	+234 mV	+213 mV	+210 mV
Potential of unalloyed T-430 steel after $PdCl_2$ immersion as indicated and subsequent 1 hr in stagnant N H_2SO_4	-515 mV	-486 mV	-491 mV	-201 mV	-205 mV	-202 mV	–
Potential of T-430 steel containing 2% Mo after $PdCl_2$ immersion as indicated and subsequent 1 hr in stagnant N H_2SO_4	-470 mV	-215 mV	-205 mV	-145 mV	–	+400 mV	–

Tomashov and coworkers (52) demonstrated the beneficial effects, similar to those mentioned above, of Cu and Pt electrodeposition upon the corrosion resistance of stainless steel in dilute H_2SO_4.

2.4.3.3. 25 Cr Stainless Steel

Since 1956 Tomashov, Chernova and their colleagues have concentrated their attention on the use of palladium additions to various stainless steels for reducing acid corrosion. Their concentration of the effect on Pd was due to both economic and availability considerations. It was found that an alloy of iron -25 per cent chromium -6 per cent nickel with 0,5 per cent palladium remains passive in 10 per cent sulphuric acid solution up to 100°C (80-83). Their findings o. an alloy of iron -25 per

cent chromium - 3 per cent molybdenum with 0,5 per cent palladium (70) led to a recommendation of this composition for use in hydrochloric acid solutions up to 1,6 per cent and temperatures up to 100°C (70,84). Tomashov also carried out investigations on the influence of palladium additions to 25 per cent chromium alloys in 30 percent sulphuric acid (Figure 2.34).

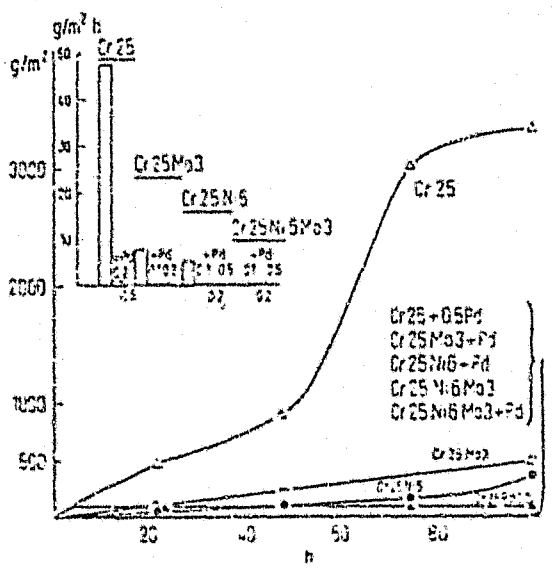


FIGURE 2.34:- The Influence of Pd alloying additions on corrosion resistance of 25% Cr steel in 30% H_2SO_4 at 20°C (85).

High chromium steels, Fe - 25 Cr - 6 Ni - 2 Mn-3 Mo - 0,85N, without Pd and with 0,2% Pd were investigated (85). The steel without Pd, unlike Fe-28 Cr steel (71), had a relatively low corrosion rate in slightly aggressive acid solutions. For this reason, the modification of this steel with 0,2% Pd does not change its corrosion resistance significantly in 1% HCl in 100°C, in 2% and 3% HCl at 20°C, in 10% and 20% H_2SO_4 at 50°C, and 10% H_2SO_4 at 100°C. In more aggressive conditions (2% HCl at 50°C and 100°C, 3% HCl at 50°C, 30% H_2SO_4 at 50°C and 20% H_2SO_4 at 100°C), this stainless steel with 0,2% Pd self-passivates and possesses a high corrosion resistance, whilst without Pd it

remains active (71).

In 1977, Tomashov et al (45, 80) described the effect of palladium additions to a duplex 25 per cent chromium - 3 per cent nickel - 2 per cent molybdenum -0,8 per cent manganese steel containing up to 1 per cent nitrogen. The alloys were made by plasma arc melting which makes it possible "to melt steels with nitrogen contents 1,5 to 2 times higher than the standard solubility level of nitrogen in steel of a specific composition at the liquidus temperature". Such nitrogen contents greatly increase the yield strength and help to make the structure completely austenitic. Additions of 0.2 per cent palladium made this alloy passive in 20 to 30 per cent sulphuric acid in the range of 20°C to 100°C, and in 1 to 3 per cent hydrochloric acid at 20°C to 50°C.

To observe the accumulation of palladium on the surface of an alloy undergoing self-passivation, Tomashov et al (80,86) carried out electron microscope studies after exposure to 10 per cent sulphuric acid at 25°C. Upon immersion in the acid the specimens were activated by cathodic polarization to initiated dissolution of the alloy. As the 25 per cent chromium alloy dissolved, palladium was concentrated on the surface until the electrode potential changed in the positive (noble) direction and the alloy became passive. On alloys with 0,2 and 0,5 per cent palladium, particle sizes in the ranges of 200 to 600 Å were measured with increasing exposure time, their number, but not their size, increased.

Figure 2.35 illustrates the influence of palladium additions on the corrosion resistance of 25 per cent Cr alloy steel in 50 per cent formic acid at 10[illegible] (70).

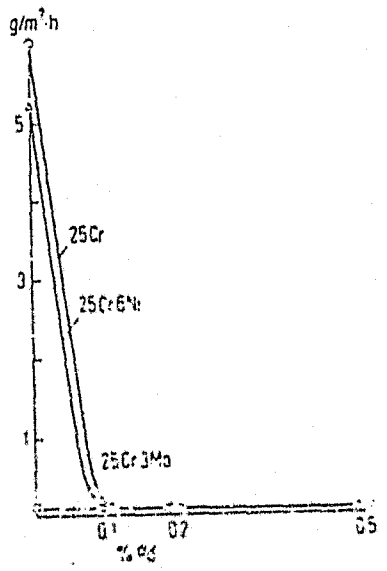


FIGURE 2.35:- The influence of Pd on corrosion resistance of 25% Cr steel in 50% formic acid at 100°C (70).

Tomashov et al also investigated the mechanical properties and corrosion properties of 25% Cr steel free from interstitial impurities (C + N) and studied the influence of 2 per cent Mo and 0,3% Pd added to the steel in various concentrations of sulphuric acid (87).

2.4.3.4. 27 Cr Stainless Steel

A basis material of higher chromium content showed a still more marked effect of noble metal additions. Figure 2.36 shows the results obtained on adding 0,5 percent platinum and 0,5 and 1,0 percent palladium to a straight 27 percent chromium steel containing no nickel.

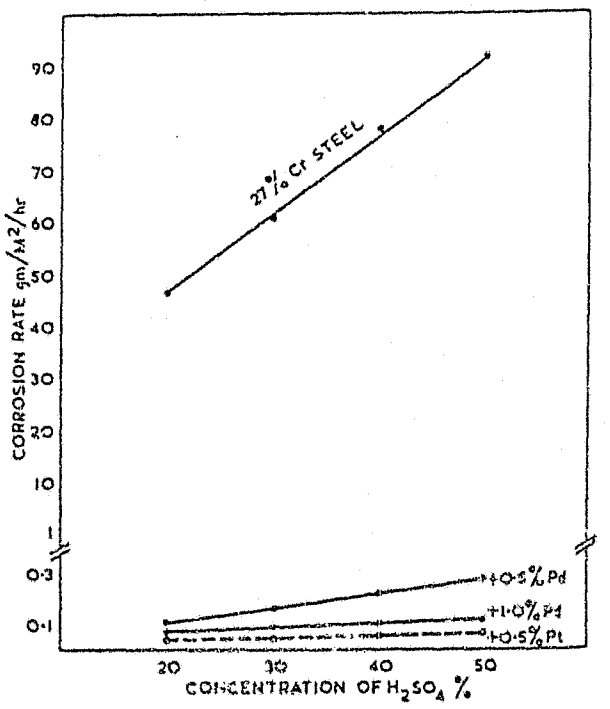


FIGURE 2.36:- Rate of corrosion of 27% Cr steel alloyed with Pt and Pd in relation to concentration of H_2SO_4 (52).

The region of corrosion resistance to sulphuric acid was higher than for the chromium-nickel steels used in other experiments (52,70). The effect of noble metal additions to 27 percent chromium stainless steel on the corrosion rate is shown by Figure 2.37.

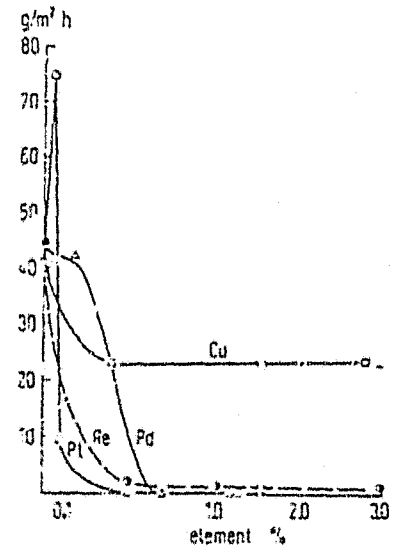


FIGURE 2.37:- The influence of alloying additions (Pt, Pd, Re and Cu) on corrosion of stainless steel (27% Cr). Investigations of stainless steel with Pt, Pd and Cu in 20% H_2SO_4; stainless steel with Re in 5% H_2SO_4 at 20°C (70).

TABLE 2.8.

Effect of Cathodic Additives Pt and Pd on the Corrosion Rate of 27% Cr Steel in Formic and Oxalic Acids at 100°C (52).

Cathodic additive	Test duration, hr	Corrosion rate, g/m². hr		
		10% Formic acid	50% Formic acid	10% Oxalic acid
Without additive	1	333	498	38.3
	10	D	D	7.8
0.1% Pt	1	0.6	75	2.3
	10	0.13	8.8	0.32
0.5% Pt	1	2.2	0.4	1.0
	10	0.11	0.05	0.12
0.7% Pd	1	1.4	3.1	1.1
	10	0.09	0.6	0.25
1.1% Pd	1	1.5	0.7	1.0
	10	0.33	0.08	0.1

Remarks: The letter "D" designates that the specimen dissolved completely. It can be assumed that in this case the rate of dissolution in 10 hr approx

Similar results were obtained for 26 percent chromium 0,5 percent

nickel steel. The noble metal additions also provided greatly increased resistance of 27 per cent chromium steel to formic and oxalic acid solutions (see Table 2.8) at 100°C (69).

2.4.3.5. 28 Cr - 4 Mo Stainless Steel

The super-ferritic iron-chromium-molybdenum alloys have superior pitting, and crevice corrosion resistance compared with Type 430 Stainless Steel. Streicher (80,88) experimented with all the platinum group metal additions to produce passivity in boiling 10 percent sulphuric acid. It was found that a 28,5 percent chromium -4,0 percent molybdenum stainless steel which is ductile and weldable, resists pitting and crevice corrosion in 10 percent ferric chloride solution up to 50°C. Unlike the austenitics, it is also resistant to stress corrosion cracking in various sodium chloride tests, as well as in the severe boiling 45 percent magnesium chloride test. To make 28 Cr - 4Mo alloy resistant to boiling 10% H_2SO_4, small amounts of the six pgm's were added as alloying elements. Some results are given in Table 2.9.

It was found (Table 2.9) that every one of these elements when present in excess of a certain minimum concentration, bring about passivation of the 28Cr-4Mo alloy in boiling H_2SO_4. The minimum concentration of the noble metal required varies with the element and is independent of atomic weights i.e. concentration of At%. The determining factors are the electrochemical properties of these elements (see Theory of Noble Metal Alloying Concept). Additions of a noble metal in a concentration lower than that required to produce passivity actually increase the corrosion rate of 28Cr - 4Mo alloy (52 180 mils/yr). This is in agreement with work done by Biefer (74) on 17Cr steel. Increasing the concentration above the minimum concentration required for passivity progressively decreased the passive corrosion rate.

TABLE 2.9

The Effect of Noble Metal Additions on the Corrosion Resistance of Iron -28.5 percent Chromium - 4.0 percent Molybdenum Alloy (88).

Noble metal addition Weight per cent		Boiling 10 per cent sulphuric acid		Pitting corrosion (a)		Stress corrosion (b)
		State	Corrosion rate, in mil/year (c)	$KMnO_4$–NaCl	$FeCl_3$	$MgCl_2$
None		active	52,180	R	R	R
Platinum	0.005	active	58,000	R	R	—
	0.006	passive	48	—	R	—
	0.20	passive	1	—	—	R
Palladium	0.01	active	74,000	—	F	—
	0.02	passive	4	—	F	—
	0.20	passive	1	F	F	R
Iridium	0.01	passive	112	R	R	—
	0.10	passive	13	R	R	R
Rhodium	0.005	passive	14	R	F	—
Osmium	0.015	active	76,600	R	R	—
	0.020	passive	26	—	R	—
Ruthenium	0.015	active	62,200	—	—	—
	0.017	active	—	—	—	—
	0.02	passive	60	R	R	R
	0.20	passive	9	—	R	R
	0.30	passive	2	R	R	R
	0.50	passive*	3	—	R	cracked in 17 h (d)

*self-repassivating R–Resistant; F–Fails

(a) 2 per cent $KMnO_4$-2 per cent NaCl at 90°C, simple immersion. 10 per cent ferric chloride, $FeCl_3 . 6H_2O$, at 50°C with crevices.
b) Boiling (155°C) 45 per cent $MgCl_2$, U-bend specimen. R-no cracking after 2400 h exposure.
(c) Thousandths of an inch per year.
d) No cracking in 26 per cent NaCl at 200°C.

In aggreement with previous investigators, the minimum concentration required to make the alloy passive on immersion in the acid solution decreases with increasing chromium content and varies from 0,005 to 0,02 wt %, depending on the noble metal used. Large amounts of noble metal additions i.e. 0,5 percent ruthenium (see Table 2.9) are required to make the alloy self-passivating.

Passivation of 28Cr - 4Mo alloy in H_2SO_4 by noble metal additions is useful only if pitting corrosion is not impaired. From the data in Table 2.8, it is apparent that palladium destroys the resistance in both pitting tests and that rhodium impairs resistance in the $FeCl_3$ test. The other four platinum group metals are without effect on pitting resistance in these tests. Additional pitting tests were made in two other halide solutions, bromine - zinc bromide and sodium hypochlorite at room temperature (Table 2.10). The bromine solution is more corrosive than $FeCl_3$, i.e. pitting occurs in both Hastelloy C and 28 Cr - 4 Mo alloy with platinum. Iridium, osmium and ruthenium do not impair pitting resistance in the bromine solution, nor does ruthenium (the only element tested) in the hypochlorite solution. Of these, ruthenium, because of its lower cost, appears to be preferred for producing resistance to acid corrosion for 28Cr - 4 Mo alloy.

TABLE 2.10

Comparison of Pitting Resistance in Halide Media (88).

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

R—Resistant; F—Fails.

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

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

2.4.3.5. 40 Cr Stainless Steel

The results of research on the electrochemical and corrosion properties of Fe-Cr (20% to 80%Cr) alloys is shown in Figure 2.38a (71).

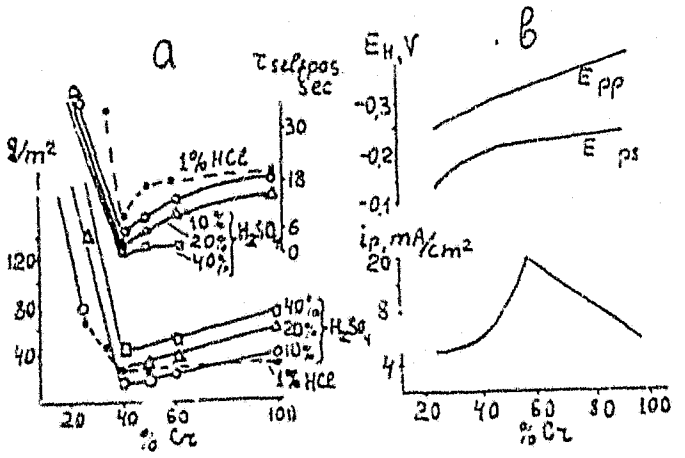


FIGURE 2.38:- Effect of chromium content: (a) on the self passivation time and weight loss of alloys with 0,2% Pd in sulphuric acid at 100°C and in boiling hydrochloric acid, and (b) on passivating characteristics of alloys, primary passivation potential (Epp) and complete passivation potential (Eps).

The Fe-40% Cr - 0,2% Pd alloy has the highest rate of self-passivation and maximum corrosion resistance (see Figure 2.38). The study of the anodic passivation kinetics suggests that in the Fe-Cr system, the passivation and complete passivation potential change slowly to move favourable (negative) region with the further increase of Cr content beyond 40%. However, the passivation current greatly increases for the alloys with more than 40% Cr (Figure 2.38b). Thus, an alloy containing about 40% Cr has the best combination of passive characteristics, the result of which is the high corrosion resistance of this alloy. For instance the Fe-40Cr-0.2Pd alloy, after cathodic activation, self-passivated in 5 to 50% H_2SO_4 at 100°C and in boiling 1% HCl. Its corrosion rate is 0,1mm/y in the passive state. The Table 2.11 shows the significant effect of cathodic alloying on the Fe-Cr system and also that the experimental alloy, 40Cr - 0,2 Pd alloy, is more resistant than several other corrosion resistance alloys (89,90).

TABLE 2.11.

Corrosion Rate K (mm/year) of Some Acid-Resistant Alloys in 40% H_2SO_4 at 100°C.

Alloy	Kh25, Kh40, Kh60:Cr (no Pd)	EI 943 (0Kh20N28M3D3T)	Hastelloy		Ti 30 Mo	Kh40 + 0.2Pd
			A, B	C		
K, mm/year	~10 000	3	0,2	3,0	0,18	0,05

Methods of protection based on passivation under conditions near the borderline between the active and passive states must always be used with caution. The maintenance of the passive film on chromium-nickel and chromium steels in acid environments depends critically on chromium content, the microstructure, the surface condition, the acid concentration and on the temperature (69).

2.5 12% CHROMIUM STEEL DESIGNATED 3CR12

The 12% chromium steels have been under extensive research and development in several countries throughout the world for several years (91-96). These corrosion resistant steels, less costly than conventional stainless steels offer a wide range of applications in the paper and pulp, chemical, construction and power generation industries (97). The development of a 12% chromium corrosion resisting steel received serious consideration in South Africa because of the availability of vast reserves of ferrochromium (98,99). Middelburg Steel and Alloys (Pty) Limited developed a new ferritic corrosion resistant steel designated 3CR12 which has far superior corrosion properties to mild steel. 3CR12 steel is based on AISI type 409 Stainless Steel. The relative nominal compositions are as follows:-

TABLE 2.12

Compositions of 12% Chromium Steels

	C	N	S	Mn	Si	Ti	Cr	Ni
AISI 409	0,08 max		0,045 max	1,0 max	1,0 max	6 x C	10,5 - 11,75	0,5 max
3CR12	0,024	0,013	0,014	0,80	0,45	0,21	11,44	0,42

The AISI 409 type is a low chromium ferritic stainless steel stabilised with titanium, available as a sheet material. This type of ferritic stainless steel suffers from two important limitations viz., inferior corrosion resistance when compared with 316 or 304 stainless steel and poor weldability. The high heat input when welding thick sections result in the formation of brittle martensite at the grain boundaries seen in the heat-affected zone. A coarse grain size combined with martensite formation results in poor impact properties. Another factor is the deleterious effect on corrosion resistance whereby intergranular corrosion is produced. The AISI type 409 stainless steel is widely used in the automobile industry for exhaust systems since the alloy resists the condensate attack from within the component and is also able to withstand the corrosive effect of salt deposits on its exterior.

The basic development of 3CR12 began within the conventional type 409 specification. Modifications were made to the chemical aimpoints in order to improve the mechanical propterties, weldability in heavy sections and hot workability (See Table 2.12). For determining the ferritizer/austenizer balance, the following formula was used.

$$\text{Ferrite Factor} = \%\,Cr + 6\%\,Si + 8\%\,Ti + 4\%\,Mo + 2\%\,Al + 4\%\,Nb - 2\%\,Mn - 4\%\,Ni - 40\%\,(C + N)$$

At values in excess of 13,5, the steel will be ferritic at all temperatures i.e. will not form martensite at the grain boundaries.

TABLE 2.13

Mechanical properties of 3CR12 (100).

PROPERTY	MINIMUM	TYPICAL
Tensile Strength, MPa	460	530
0,2% Proof Stress, MPa	280	380
Elongation (in 50mm), %	20	26
Hardness, Brinell	220 (max)	165
Charpy Impact Energy (20°C), J	50	80

The carbon and nitrogen content, as well as the ferrite factor influence the mechanical properties of the 3CR12 steel (see Table 2.13). Carbon, nitrogen and nickel increase the hardness and strength of the steel because of the increase in martensite formed from the austenite during cooling and also some solution hardening (101).

In the transverse direction, 3CR12 suffers from anisotropy and poor ductility so that an annealing treatment is required (99, 101). The laminations are due to intergranular decohesion, common to hot rolled duplex steels.

The low chromium content of 3CR12 causes the passive film to form rather slowly and discontinuously on the surface. Therefore it is essential to passivate 3CR12 in dilute nitric acid before service in a corrosive environment otherwise pitting can take place (102). 3CR12 is not subject to stress corrosion cracking in chloride, nitrate or hydroxide solutions (103), but stress-accelerated corrosion cracking occur in H_2S environments.

Briggs and Parker (104) have shown that the Super 12% chromium steels has better oxidation resistance than lower chromium steels. Investigations are at present in progress on the high temperature corrosion of a 12% chromium steel (101).

The prerequisite for an alloy to be commercially viable is for it to be weldable. Austenitic electrodes of 308, 309 or 316 type were initially used in manual metal arc (MMA) welding of 3CR12 plate. Due to the high chromium content of these filler metals, there were marked differences in the mechanical properties of the depositied weld metal, heat-affected zone and parent plate. Another factor to be considered is chromium contents resulting in the setting up of a galvanic couple between parent plate and filler metal.

At present a consumable electrode, Transarc E 3CR12 has been developed at the University of Witwatersrand which is compatible with the parent metal in terms of mechanical and corrosion properties.

3. EXPERIMENTAL PROCEDURE

3.1. Production of the Experimental Alloys

3.1.1. General

The 3CR12 alloy was used as a basis in this study. Three series of alloys were prepared viz., 3CR12-Pd, 3CR12-Ru and 3CR12-Pt. In the case of the 3CR12-Pd and 3CR12-Ru alloys, the platinum group metal addition aimpoints were 0,05, 0,1, 0,2 and 0,5%. However in the case of the 3CR12-Pt alloy the platinum levels of 0,05, 0,1, 0,2, 0,25 and 0,5% were carried out.

In order for the study to be more comprehensive, a second batch of alloys had to be made up containing the same level of platinum group metal additions as described previously.

3.1.1.2. Melting Procedure

Melting of the alloys were carried out in a high-frequency 5kg induction furnace with a argon hood to prevent the contamination by carbon, nitrogen and oxygen from the atmosphere.

The 3CR12 alloy was initially made up from the ferrochromium and various other additions to give the desired composition. A sample of the 5kg ingot produced was analysed to determine whether or not the aimpoints were achieved. A split heat technique was then used to make a 1kg ingot from a 5kg heat. Alloy composition adjustments were made to the 1kg heat.

3.1.1.3. Processing

The 1kg ingot were heated for 40 minutes at 1150°C then rolled down to a 14mm thick plate. The finishing temperature was in the region of 700°C. The ingots were heat treated in the annealing furnace at 760°C for 40 minutes then air-cooled.

The second batch of alloys followed a similar processing procedure but were rolled down from 19mm to 7mm.

3.1.1.4. Microstructure

Since the heat treatment of the 3CR12 alloys were expected to be the same, viz., heat treatment at 760°C for 40 minutes followed by air cooling should produce a ferritic microstructure. Specimens were mounted, polished and etched in Villela's reagent for metallographic examination.

3.1.1.5. Impact Testing

From the first batch of alloys, the Transverse Standard Charpy V-notched (CVN) impact samples were machined from the heat treated plate. In the second batch of alloys subsize CVN impact samples in the transverse direction had to be used. All the impact testing was carried out at + 21°C.

3.2. Corrosion Tests

3.2.1. Potentiodynamic Scans

3.2.1.1. General Corrosion Tests

The electrodes for the polarization studies with the Princeton Applied Research potentiostat microprocessor (see Figure 3.1) were in the form of cylinders (0,9cm x 1,30cm) machined from as-received slabs. The electrodes were polished down to a 1000 grit finish, ultrasonically cleaned in ethyl alcohol and washed with distilled water. An electrode (specimen) is mounted on the electrode holder and placed in a polarization cell containing either 1N H_2SO_4 maintained at 30°C or 1N H_3PO_4 at 60°C. The argon was continuously bubbled through the solution for de-aeration and agitation. The electrode potentials were measured relative to a saturated calomel electrode (SCE) with a Luggin-Haber probe.

The specimens were allowed to stabilize for 1 hour in the solution at 30°C before scanning as specified by ASTM-G5. For the anodic polarization, scanning was started 100 millivolts below the open-circuit potential and a sweep rate of 200 μV/s used to 1,2 volts. Potentiodynamic polarization curves were obtained in duplicate for each specimen with fairly good reproducibility. Also a resistance polarization plot was run choosing 20 millivolts on eitherside of the corrosion potential to calculate the corrosion rate of the specimen. The passive range of each alloy was taken at 100 $\mu A/cm^2$.

3.2.1.2. Pitting Tests

Potentiodynamic scans were carried out on an Amel Metalloscan potentiostat (see Figure 3.2). The specimens were subject to the same conditions used in the general corrosion test in terms of preparation and cleaning procedure. For the pitting corrosion, the scanning was started 20 millivolts below the open circuit potential at a sweep rate of 200 μV/s to 10^3 μA and then reversed scanned back to the protection potential.

The pitting potential of each specimen in 0,1N Na 1 was taken at 10 $\mu A/cm^2$. Reproducibility of the potentiodynamic curves was not as good as in the case of general corrosion so that five scans per alloy were carried out.

3.2.1.3. Wood Pulp Liquor Tests

The potentiodynamic polarization curves were carried out in quadriplicate.

FIGURE 3.1:- The Princeton Applied Research potentiostat microprocessor.

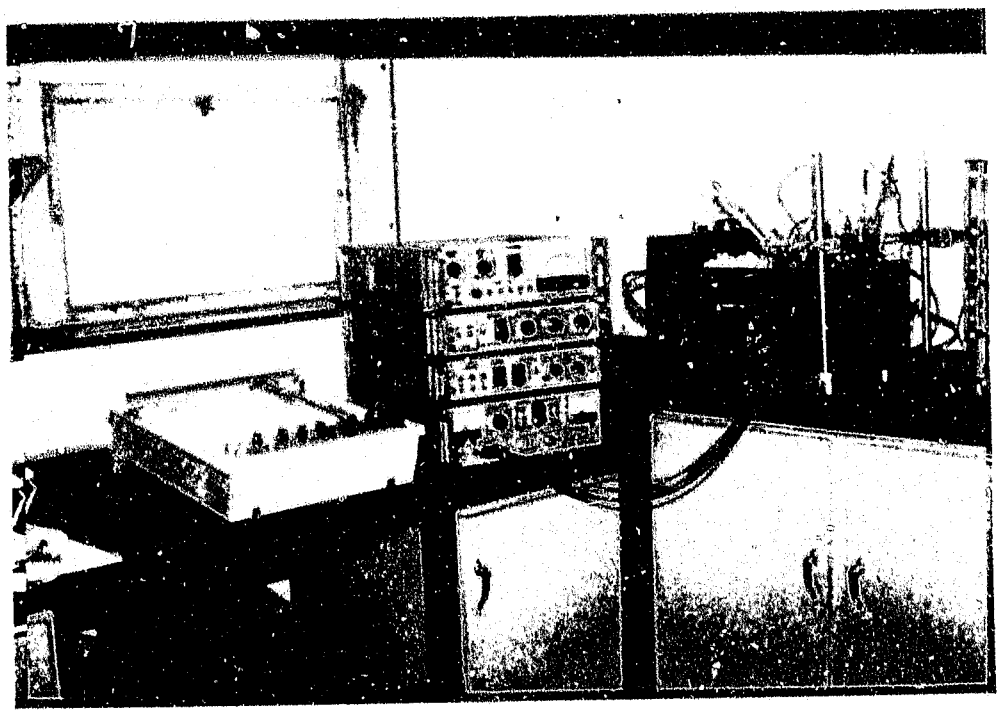


FIGURE 3.2:- The Amel Metalloscan potentiostat with the electrochemical cell.

3.2.2. Total Immersion Tests

The dimensions of the test coupons for the first batch were 2,5cm x 2,5cm x 3mm whilst for the second batch they were 1,5cm x 1,5cm x 3mm. The coupons were polished to a 800 grit finish degreased ultrasonically in chloroform and left to air dry. They were then weighed then placed in a test solution under stagnant conditions at 60°C (see Figure 3.3). After the immersion, each test coupon was cleaned under running water using a mildly abrasive soap and brushing them then ultrasonically degreased in chloroform followed by weighing them.

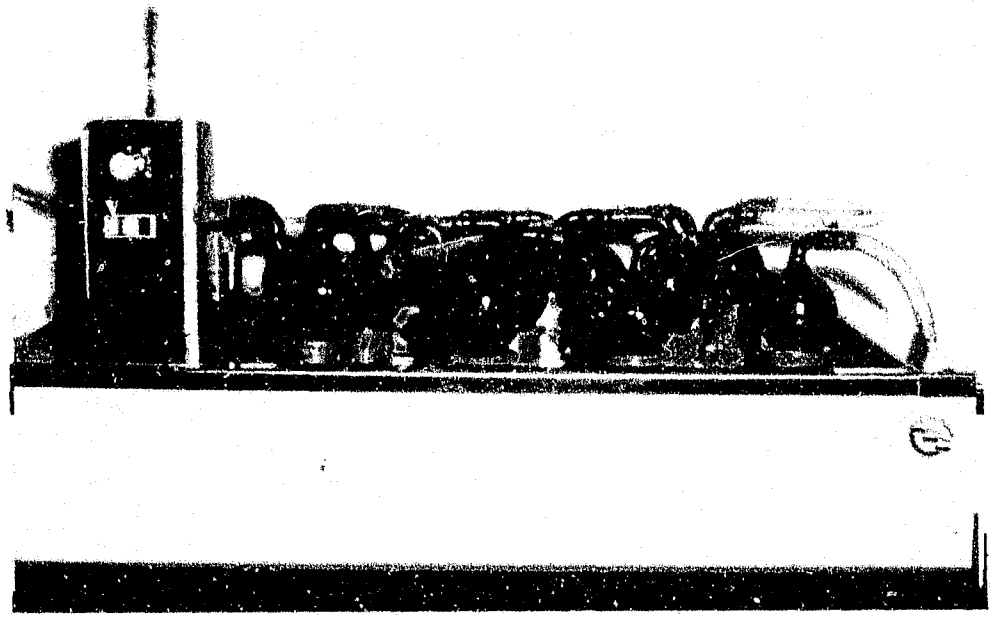


FIGURE 3.3:- A view of the immersion test in a thermostatically controlled oil bath.

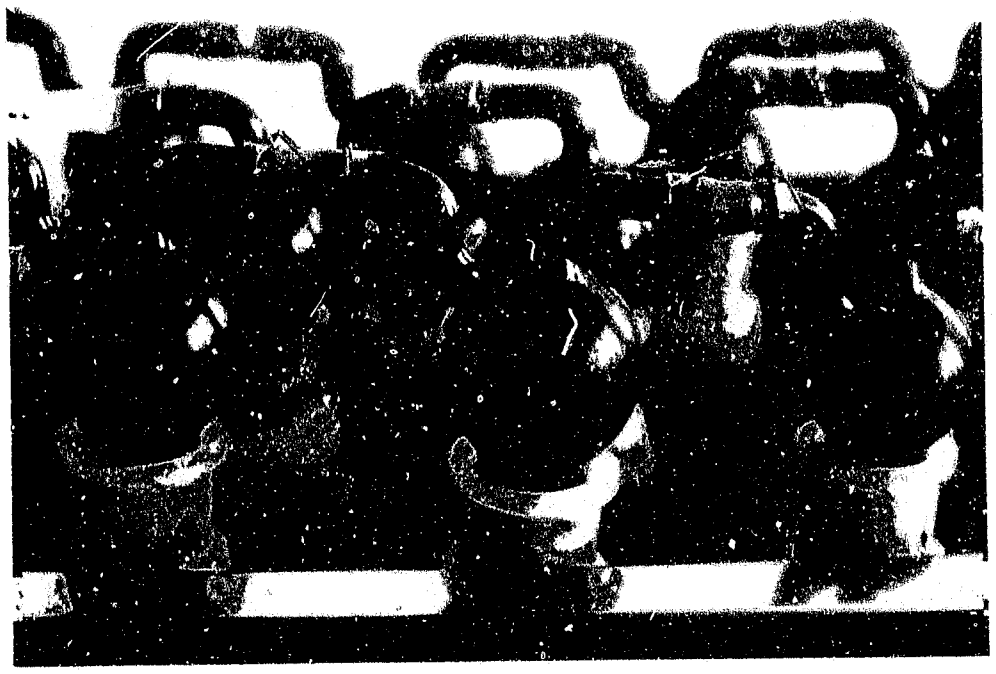


FIGURE 3.4:- A close-up view of the Halar coated condensers and polypropylene flasks.

3.2.2.1 General Corrosion

These immersion tests were carried out in two inorganic acids, viz., 1N H_2SO_4 at 30°C and 1N H_3PO_4 at 60°C. The tests duration for the 1N H_2SO_4 was 72 hours, whilst for the 1N H_3PO_4, the test duration was 240 hours.

3.2.2.2. Wood Pulp Liquors

There were four sets of woodpulp liquors i.e. two green liquors from Soda and Krafts processes and two weak black liquors from Soda and Kraft processes. The immersion tests were run in polypropylene flasks with Halar coated cold finger condensers because of the basicity of the liquors (see Figure 3.4). The tests were run at 60°C thermostatically controlled in oil baths.

3.2.2.3. Orange Free State Mine Water (Geduld Gold mine).

Total immersion corrosion tests were conducted at 60°C for 90 days. Weight loss and the corrosion rate was calculated as mdd for each alloy.

4. RESULTS AND DISCUSSION

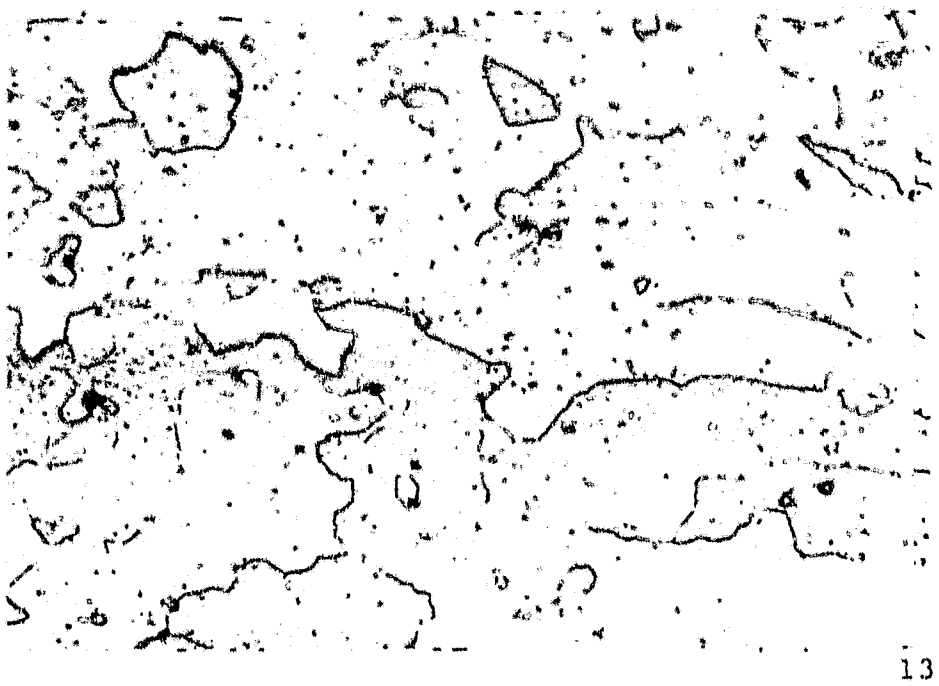
4.1. 12% Chromium - Platinum Group Metal Alloys

4.1.1. General

Two batches comprises, 15 heats in all; the first fifteen heats of 1kg each were used for potentiodynamic testing in 1N H_2SO_4, 0,1N NaCl, the four wood pulp liquors, also total immersion testing, and Charpy impact testing. The other alloys were tested in 1N H_3PO_4 (both potentiodynamic and total immersions), 1N H_2SO_4 (total immersions), O.F.S. minewater (total immersions), and were also tested for subsize Charpy tests.

4.1.2. Composition

All the alloys were analysed on a PAR x-ray spectrometer and the carbon and nitrogen levels were determined on a Leco analyser. The platinum group metals in the alloys were analysed separately and were found to be in good agreement with the aimpoints (see Tables 4.1 and 4.2). In the case of the second batch of heats, the F4 alloy was found to have a high carbon level. A probable reason could be that the ruthenium addition increased the temperature of the steel in the furnace resulting in the attack on the cast iron mould with the resultant contamination of the molten metal.



130X

FIGURE 4.1:- Microstructure of H1 alloy

4.1.3. Microstructure

As can be seen in figure 4.1, the alloys all show a typical ferritic microstructure.

TABLE 4.1

COMPOSITIONS OF FIRST BATCH OF 3CR12-PGM ALLOYS

CODE	C	N	S	Mn	Si	Ti	Cr	Ni	Pd	Ru	Pt
D1	0,021	0,015	0,009	1,200	0,410	0,20	11,17	0,61			
A1	0,018	0,014	0,0075	1,157	0,466	0,32	11,27	0,60	0,05		
A2	0,017	0,013	0,0017	1,166	0,474	0,25	11,09	0,59	0,10		
A3	0,016	0,015	0,0071	1,189	0,500	0,19	11,09	0,59	0,20		
A4	0,018	0,016	0,0073	1,187	0,501	0,135	10,86	0,66	0,50		
B1	0,014	0,015	0,0080	1,391	0,461	0,32	11,11	0,67		0,05	
B2	0,014	0,016	0,0078	1,428	0,479	0,26	11,12	0,67		0,10	
B3	0,014	0,018	0,0080	1,409	0,484	0,22	10,97	0,66		0,20	
B4	0,015	0,020	0,0078	1,437	0,530	0,18	10,85	0,67		0,50	
C1	0,016	0,015	0,0092	1,277	0,459	0,36	11,39	0,62			0,05
C2	0,015	0,014	0,0086	1,292	0,469	0,35	11,40	0,62			0,10
C3	0,017	0,018	0,0080	1,285	0,473	0,30	11,29	0,62			0,20
C4	0,017	0,018	0,0086	1,268	0,481	0,24	11,11	0,62			0,25
C5	0,021	0,029	0,0105	1,106	0,308	0,40	11,17	0,60			0,20
C6	0,022	0,026	0,0125	1,079	0,356	0,37	10,66	0,58			0,50

TABLE 4.2

COMPOSITION OF SECOND BATCH OF 3CR12-PGM ALLOYS

CODE	C	S	P	Mn	Si	Ti	Cr	Ni	Pd	Ru	Pt
H1	0,015	0,009	0,021	1,07	0,33	0,41	11,48	0,52			
E1	0,014	0,009	0,020	1,07	0,36	0,42	11,44	0,52	0,05		
E2	0,013	0,009	0,021	1,07	0,34	0,40	11,42	0,52	0,10		
E3	0,013	0,010	0,022	1,06	0,34	0,32	11,28	0,52	0,20		
E4	0,017	0,009	0,021	1,04	0,34	0,25	11,27	0,52	0,50		
I1	0,021	0,008	0,022	1,21	0,40		11,33	0,52			
F1	0,022	0,009	0,021	1,19	0,42	0,49	11,50	0,52		0,05	
F2	0,028	0,009	0,021	1,19	0,43	0,50	11,46	0,52		0,10	
F3	0,027	0,009	0,022	1,19	0,43	0,50	11,48	0,52		0,20	
F4	0,037	0,009	0,021	1,18	0,44	0,44	11,26	0,52		0,50	
G1	0,016	0,010	0,020	1,13	0,39	0,46	11,40	0,52			0,05
G2	0,018	0,010	0,021	1,11	0,39	0,47	11,30	0,52			0,10
G3	0,018	0,009	0,022	1,11	0,39	0,49	11,24	0,51			0,20
G4	0,019	0,009	0,021	1,11	0,39	0,50	11,35	0,52			0,250
G5	0,016	0,009	0,020	1,13	0,39	0,49	11,44	0,52			0,50

TABLE 4.3

IMPACT ENERGY (J) VALUES OF SUBSIZE V-NOTCHED SPECIMENS AT 21°C

CODE	ALLOY	CHARPY 1	CHARPY2	CHARPY 3	CHARPY 4
H1	3CR12	72	29	70	58
E1	3CR12 - 0,05Pd	65	90	80	90,5
E2	3Cr12 - 0,1 Pd	76,5	55	75	71,5
E3	3CR12 - 0,2Pd	89,5	104	103	114
E4	3CR12 - 0,5 Pd	100	89	82	79
I1	Unstablised 3CR12	136	60	63,5	47
F1	3CR12 - 0,05Ru	35	87	84	50
F2	3CR12 - 0,1Ru	75,5	77	79	89
F3	3CR12 - 0,2Ru	88	66,5	62,5	74,5
F4	3CR12 - 0,5Ru	86,5	78	76	78
G1	3CR12 - 0,05Pt	82	24	18	12
G2	3CR12 - 0,1Pt	60	60	10	20
G3	3CR12 - 0,2Pt	74	11	12,5	16
G4	3CR12 - 0,25Pt	25	94	84	19
G5	3CR12 - 0,5Pt	104	24,5	91	51,5

4.1.4. Impact Properties

The first batch of impact test results were discarded because of a dendritic structure due to an insufficient reduction, viz., 26%. Aslund (105) showed that a cold reduction of 85% of the low interstitial ferritic chromium steels gave very good impact toughness. The second batch of alloys was thus subjected to a 63% reduction. This lead to a great improvement in the impact toughness values (See Table 4.3). The delaminations (101) were also observed in the subsize Charpy V-notched specimens (see Figure 4.2). The 3CR12 - Pt alloys had poor subsize CVN values which is due to the inclusions and the cleanliness of the steel which resulted in a characteristic brittle failure (106). The fracture surfaces of the 3CR12 - Pd and 3CR12 - Ru alloys microscopically exhibited both brittle and ductile features (see Figures 4.3, 4.4, and 4.5). In addition, the impact toughness values of these alloys are more consistent than the 3CR12 - Pt alloys.

16,5X

FIGURE 4.2:- Fracture Surface of subsize CVN specimen (F2 alloy)

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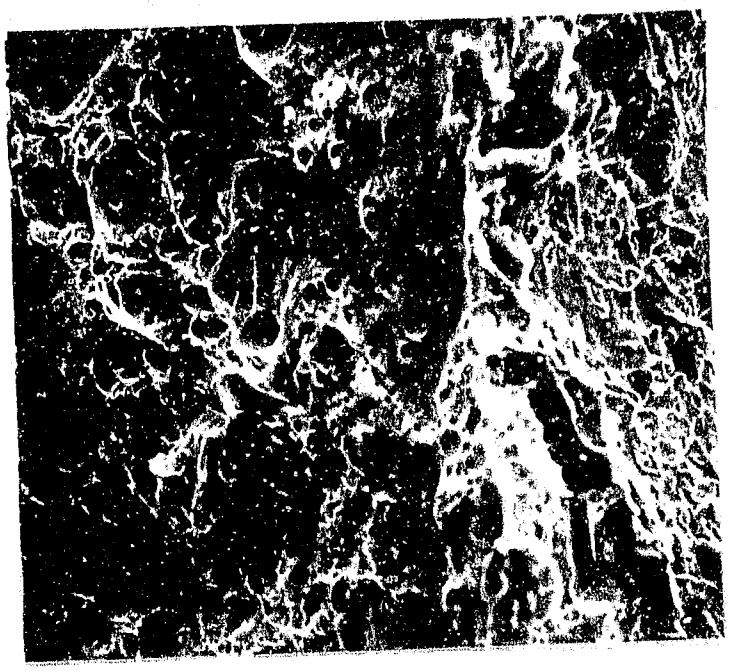
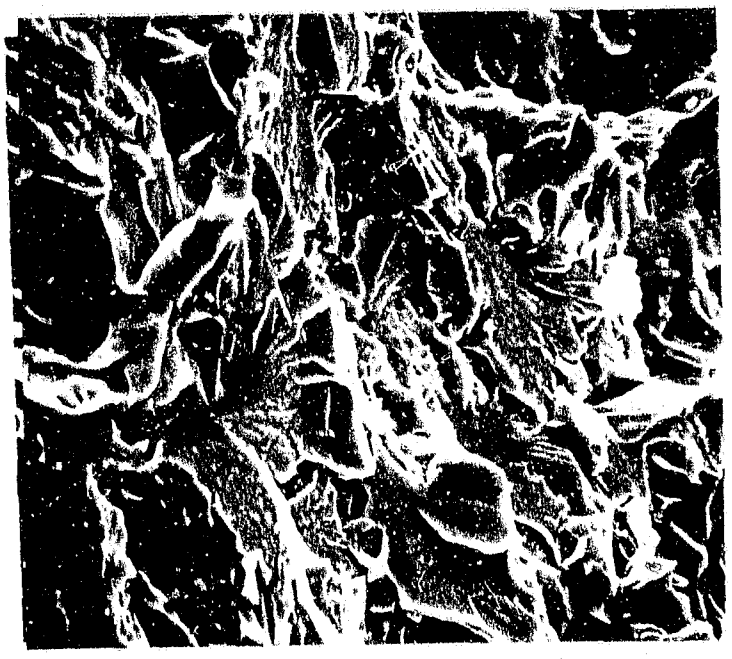
16,5X

FIGURE 4.2:- Fracture Surface of subsize CVN specimen (F2 alloy)



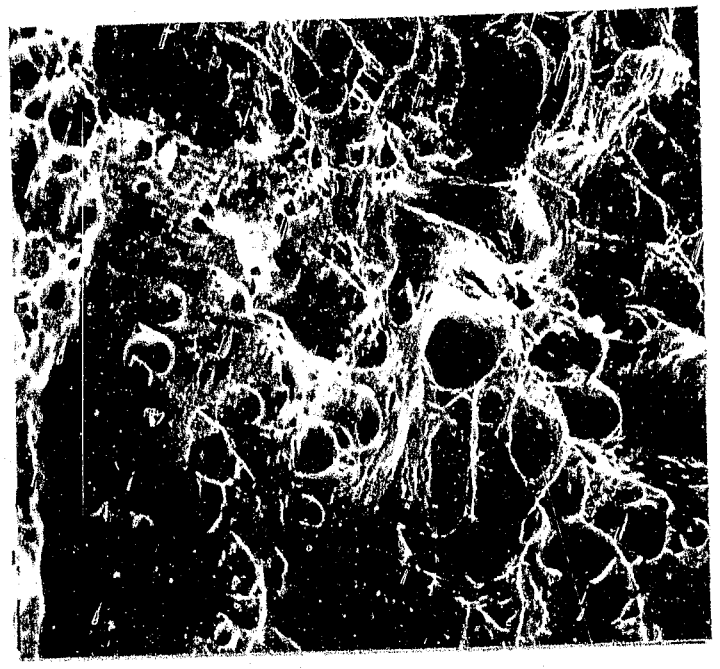
400X

FIGURE 4.3:- Fracture surface of E2 alloy with characteristic dimple ductile features on lhs and brittle cleavage features on rhs of SEM micrograph.



800X

FIGURE 4.4:- Magnified view of the E2 alloy's brittle features showing cleavage planes.



800X

FIGURE 4.5:- Magnified view of E2 alloy's ductile features showing dimples.

4.2. Corrosion Testing

4.2.1. 1N H_2SO_4

4.2.1.1. Potentiodynamic Testing

The freely corroding potential of 3CR12 is -0,509 volts [vs saturated calomel electrode (SCE)]. It can be seen from Table 4.4 that the corrosion potential of these alloys are shifted in the noble direction. The reason being that the noble metal additions strongly influence the matrix alloy with a result that the corrosion potential become more noble. This is in agreement with the work done by Tomashov (see Figure 2.13). 3CR12 steel has a passive zone of 1,054 volts, which is reduced to only 0,472 volts with the addition of 0,5% palladium (see Table 4.4). Figure 4.6 shows the influence of palladium on the primary passivation potential (Epp) and the critical current density (i_c). A 0,2% palladium addition to the 3CR12 steel increases

the Epp in the noble direction, whilst i_c has remained almost constant. At the maximum addition of only 0,5% palladium, i_c drops to 5,4 mA/cm^2 compared to 11mA/cm^2 for 3CR12 steel.

It should be noted that an addition of only 0,05% pgm, does not enhance the passive stability, since the pgm at this low concentration increases the corrosion resulting in a higher corrosion rate (68). At the low concentration of pgm, the maintenance of passivity is thermodynamically unfavourable since the matrix alloy cannot be polarised by the cathodic additions. For example, the corrosion rate of the 3CR12-Pd alloys has not been decreased but has increased due to an insufficency of palladium (see Figure 4.6). Biefer (74) found that for Type 430 stainless steel, 0,99% Pd was required to bring about a noticeable decrease in the corrosion rate.

TABLE 4.4

RESULTS OF POTENTIODYNAMIC TESTING

ALLOY	E_{corr} (VOLTS vs SCE)	PASSIVE RANGE (VOLTS)
D1	-0,509	1,054
A1	-0,499	1,050
A2	-0,476	1,063
A3	-0,450	1,023
A4	-0,396	0,472
B1	-0,427	1,005
B2	-0,311	1,036
B3	-0,300	1,045
B4	-0,289	1,023
C1	-0,436	0,932
C2	-0,414	0,468
C3	-0,282	1,059
C4	-0,285	1,063
C5	-0,289	1,046
C6	-0,280	1,063

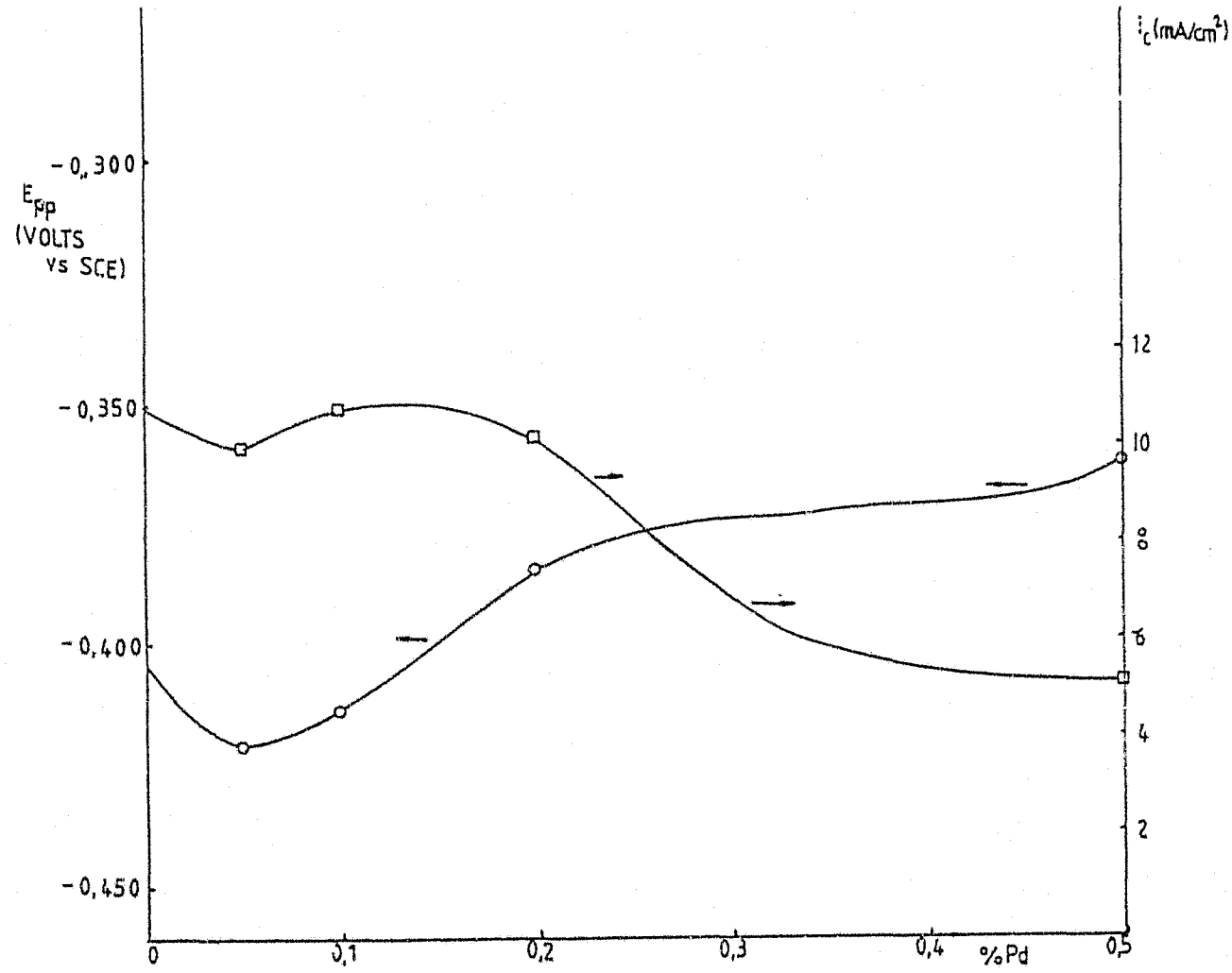


FIGURE 4.6:- The effect of palladium additions in 3CR12 steel on the primary passivation potential (Epp) and the critical current density (i_c) in 1 N H_2SO_4 at 30°C.

Table 4.4 shows the variation of E_{corr} with ruthenium alloying addition which again highlights the fact that the microcathodic alloying elements such as ruthenium shifts E_{corr} in the noble direction. The magnitude of the passive range is substantially unchanged. The influence of the ruthenium additions on the Epp and i_c can be seen in Figure 4.7. The Epp levels off at ruthenium level 0,1%. Additions in excess of 0,1% ruthenium results in a constant i_c minimum of 0,6mA/cm^2. One can

therefore conclude that 0,2% ruthenium alloying addition in 3CR12 steel would be the optimum amount for contribution to a reduced corrosion rate (see Figure 4.7). Figure 4.8 shows that 0,2% ruthenium addition results in a corrosion rate of 465 mpy.

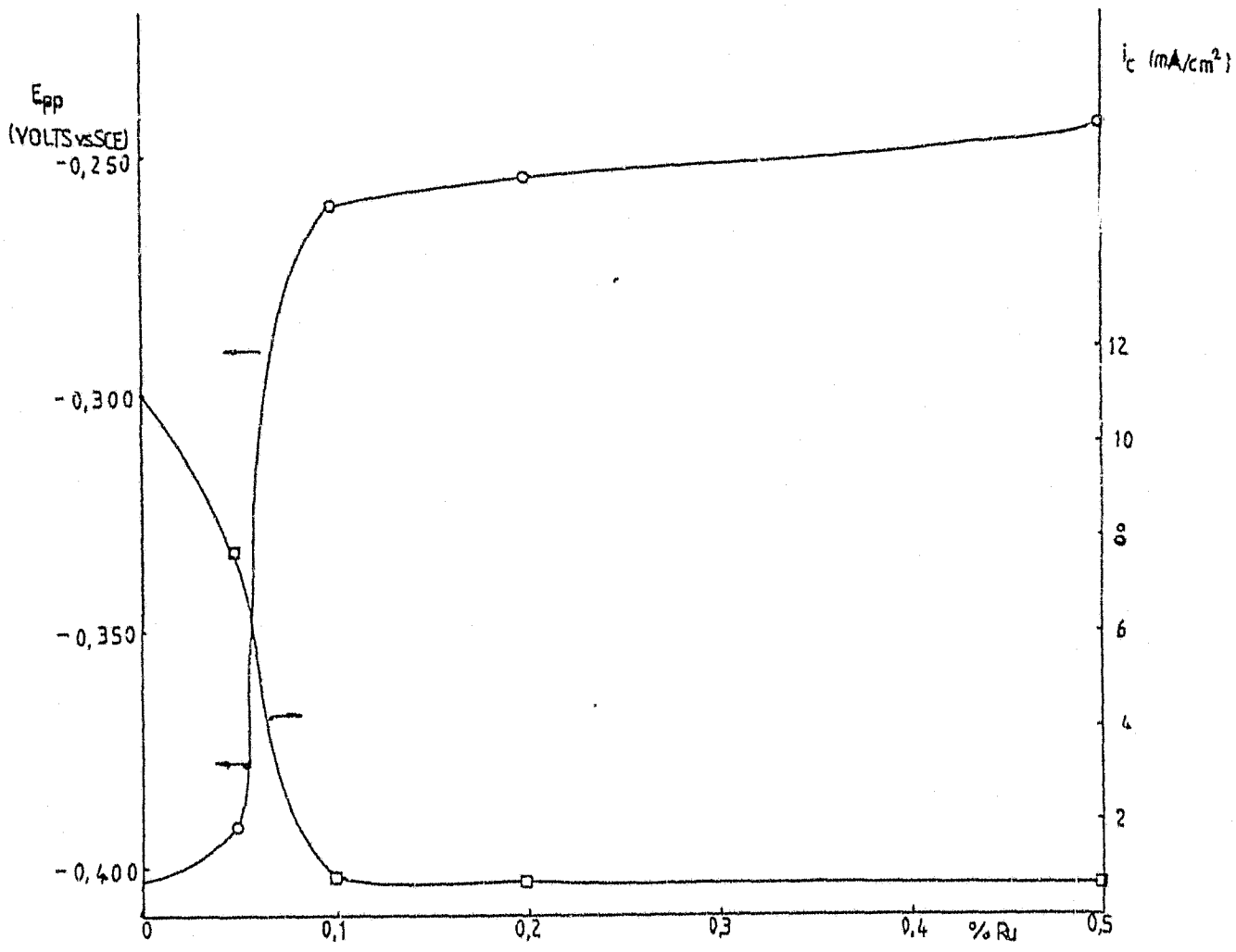


FIGURE 4.7. The effect of ruthenium additions in 3CR12 steel on the primary passivation potential (Epp) and the critical current density (i_c) in 1N H_2SO_4 at 30°C.

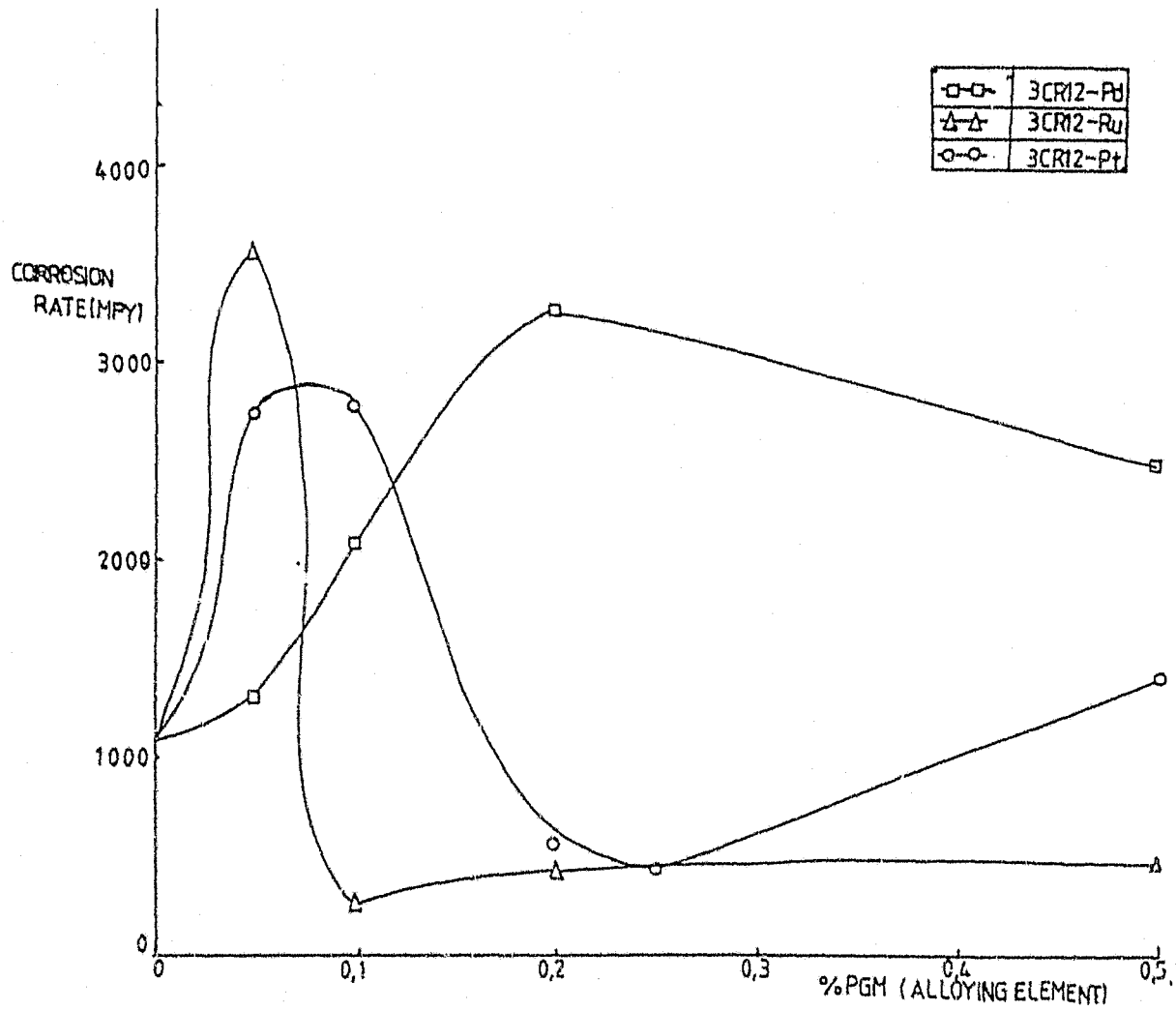


FIGURE 4.8:- The corrosion rate of 3CR12 steels alloyed with platinum group metal additions in 1N H_2SO_4 at 30°C.

According to Tomashov (65) these are two possible ways for active dissolution of the alloy to be inhibited by the ruthenium addition present in it:-

1. Blocking by the stable atoms of ruthenium of the most active sites of the crystal lattice of the alloy.

2. Reduction of the active anodic surface of the alloy due to gradual accumulation of the ruthenium particles and bubbles of molecular hydrogen on the surface.

Platinum alloying element has the strongest effect on the Ecorr (see Table 4.4.). The passive range of the 3CR12-Pt alloys generally remain constant with a few exceptions as can be seen in Table 4.4.

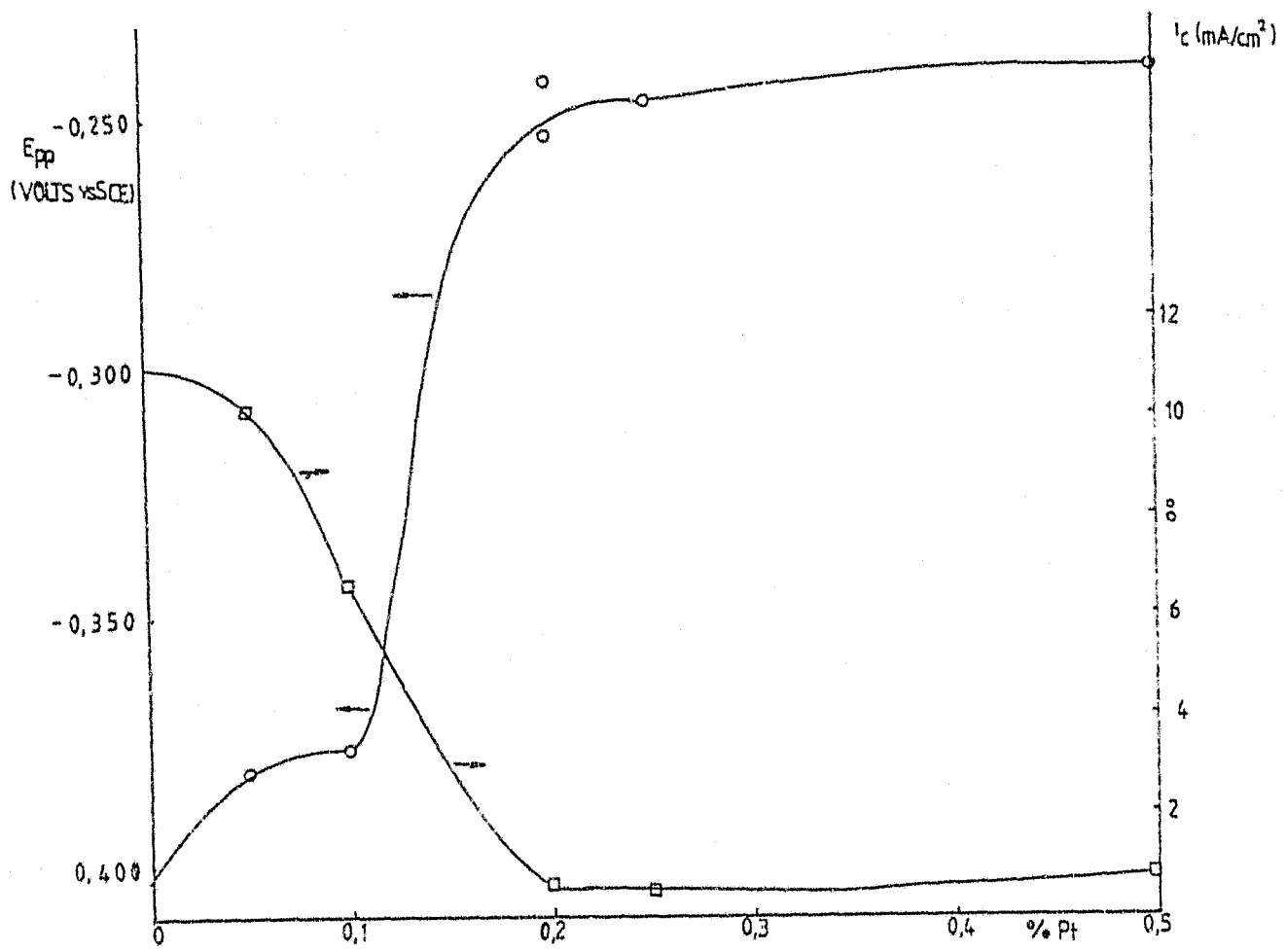


FIGURE 4.9:- The effect of platinum additions in 3CR12 steel on the primary passivation potential (Epp) and the critical current density (i_c) in 1N H_2SO_4 at 30°C.

Figure 4.9 shows the effect of platinum alloying additions in 3CR12 steel on the Epp and the i_c. As can be seen Epp remains constant at -0,250 volts after a 0,2% Pt alloying addition, whilst i_c reaches a minimum at 0,6mA/cm^2.

The corrosion rate of the 3CR12-Pt alloys attain a maximum at approximately 0,075% Pt alloying addition and reaches a minimum corrosion rate at 0,25% Pt alloying addition (see Figure 4.8). Of the three series of alloys investigated, the influence of the ruthenium addition is superior to that of either platinum or palladium additions.

4.2.1.2. Total Immersion Testing

The thickness loss of the 3CR12 alloys correlated very well with the corrosion rate obtained by linear resistance polarization studies (see Figure 4.8 and 4.10). The 3CR1 -Pd alloys also have poor corrosion resistance properties when compared to 3CR12-Ru and 3CR12-Pt alloys. From the results of immersion tests, the optimum amount of ruthenium alloying addition in 3CR12 steel is 0,2%. Which is in full agreement with the results of the potentiodynamic test. Similarly, the 0,25% Pt alloying addition in 3CR12 steel results in a minimum thickness reduction (see Figure 4.10), which correlates well with the potentiodynamic determination.

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4.2.1.2. Total Immersion Testing

The thickness loss of the 3CR12 alloys correlated very well with the corrosion rate obtained by linear resistance polarization studies (see Figure 4.8 and 4.10). The 3CR12-Pd alloys also have poor corrosion resistance properties when compared to 3CR12-Ru and 3CR12-Pt alloys. From the results of immersion tests, the optimum amount of ruthenium alloying addition in 3CR12 steel is 0,2%. Which is in full agreement with the results of the potentiodynamic test. Similarly, the 0,25% Pt alloying addition in 3CR12 steel results in a minimum thickness reduction (see Figure 4.10), which correlates well with the potentiodynamic determination.

The corrosion rate of the 3CR12-Pt alloys attain a maximum at approximately 0,075% Pt alloying addition and reaches a minimum corrosion rate at 0,25% Pt alloying addition (see Figure 4.8). Of the three series of alloys investigated, the influence of the ruthenium addition is superior to that of either platinum or palladium additions.

4.2.1.2. Total Immersion Testing

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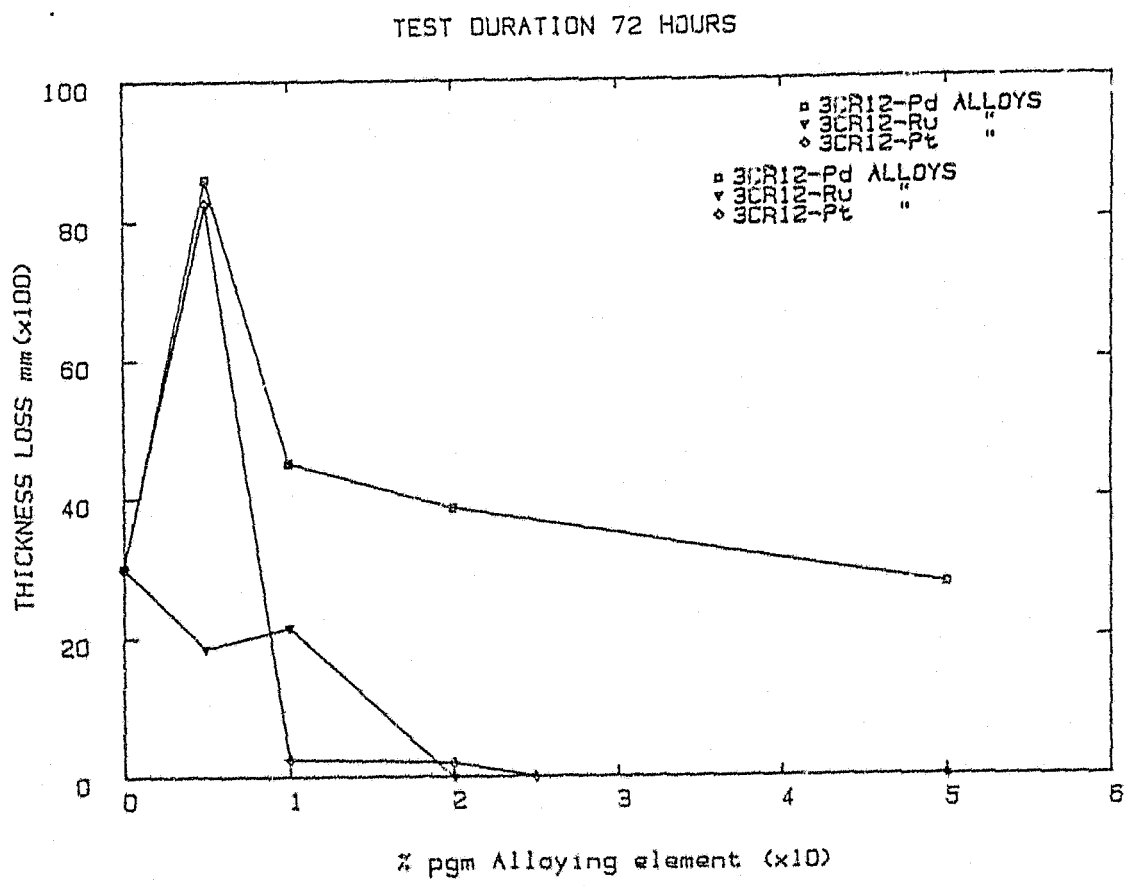

FIGURE 4.10:- The thickness loss of the 3CR12-pgm alloy immersion coupons in 1N H_2SO_4 at 30°C.

4.2.2. 0,1N NaCl

4.2.2.1. Potentiodynamic Testing

As can be seen in Table 4.5, 3CR12 alloy has a pitting potential of -0,055 volts. The addition of the palladium generally does not seem to improve the pitting resistance except for 0,1% and 0,2% palladium alloying additions respectively (see Figure 4.11) which show more noble pitting potentials.

At ruthenium levels in excess of 0,05%, the pitting resistance improves significantly. Figure 4.12 shows that 0,05% ruthenium alloying addition gives a more active pitting potential which may result in poor pitting resistance. Therefore the amount of cathodic addition in the steel influence the electrochemical parameters drastically. The effect of platinum alloying additions to 3CR12 alloys follows a similar trend to the 3CR12-Ru alloys (see Figure 4.13). The addition of 0,25% Pt results in a higher pitting potential compared to the rest of the alloys. A

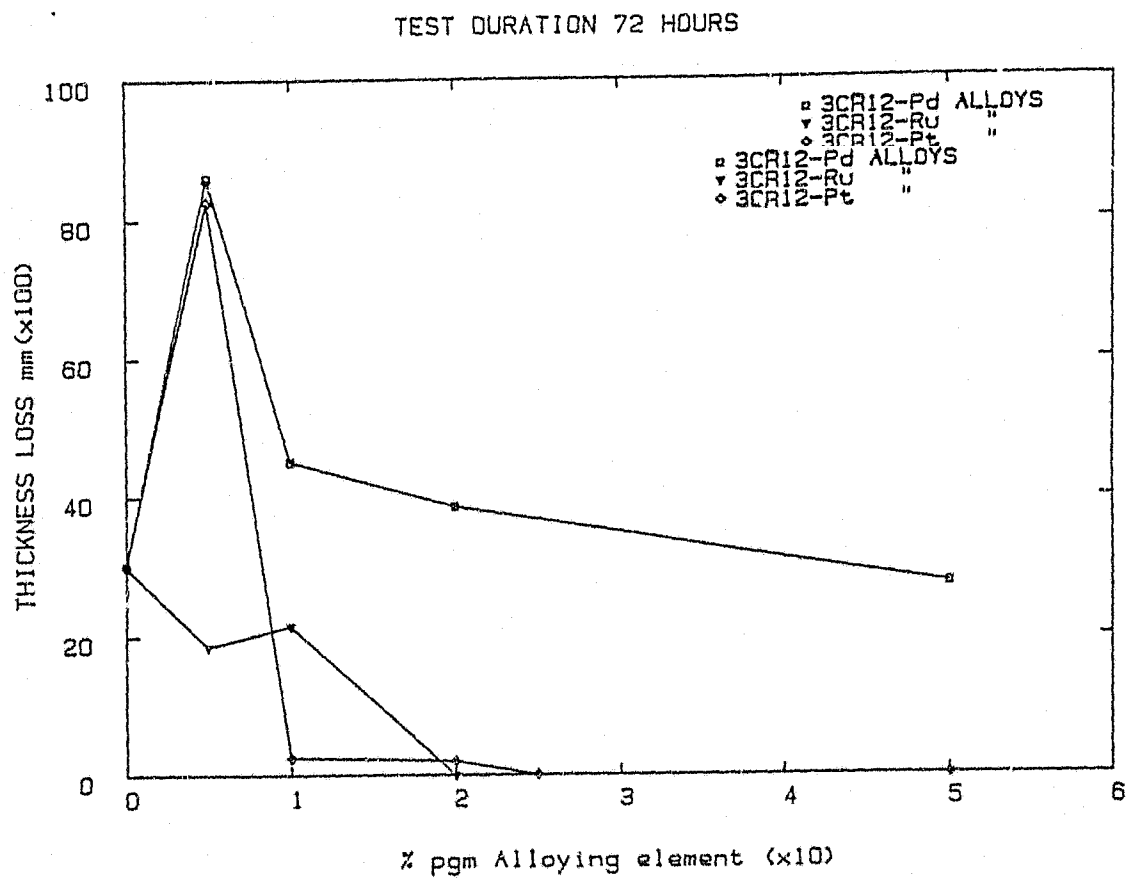

FIGURE 4.10:- The thickness loss of the 3CR12-pgm alloy immersion coupons in 1N H_2SO_4 at 30°C.

4.2.2. 0,1N NaCl

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0,1% Ru addition and 0,25% Pt addition in 3CR12, respectively give very noble pitting potentials (see Figures 4.12 and 4.13). Table 4.5 shows that there is no clear correlation between protection potential and the quantity of pgm alloying element added.

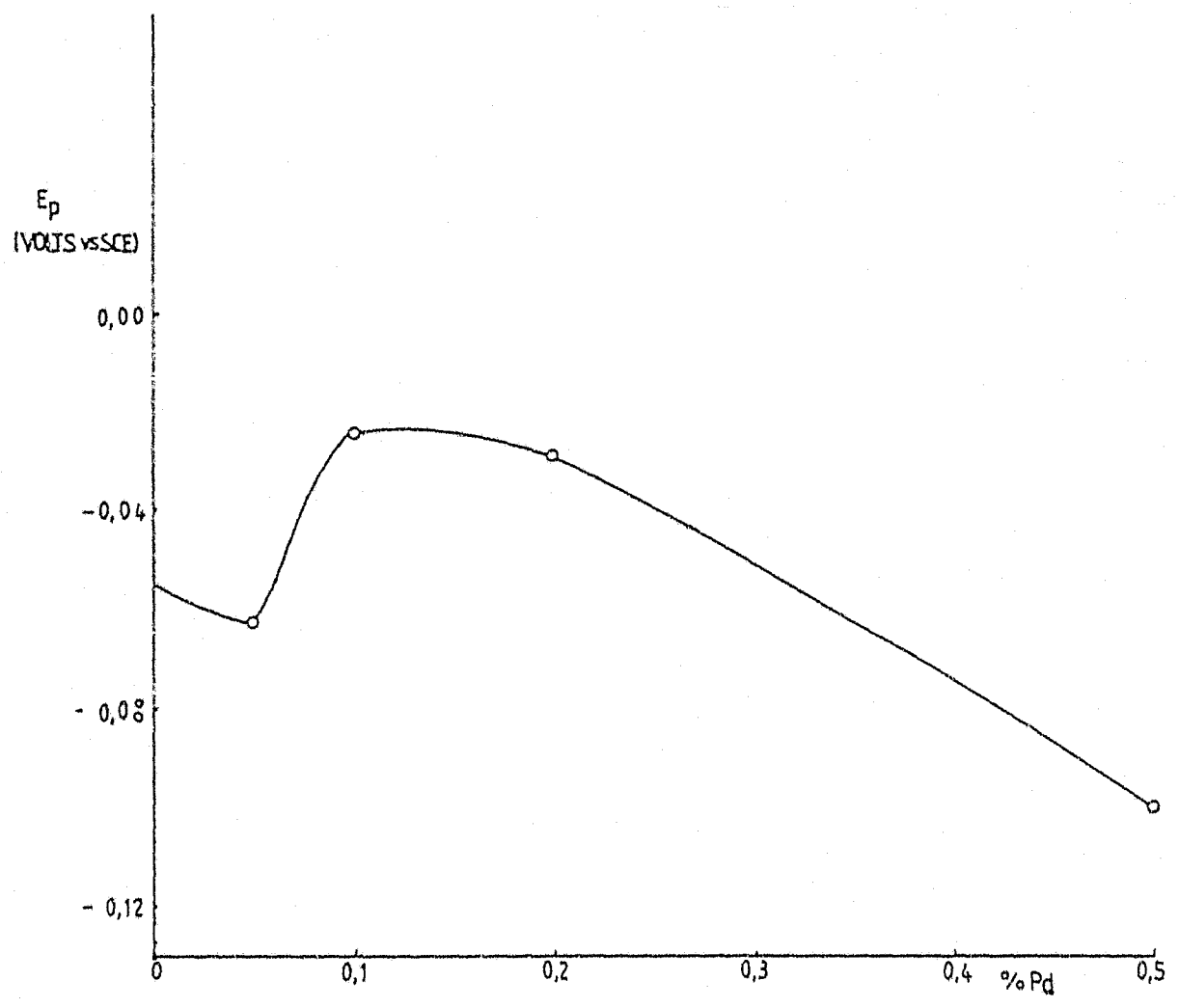

FIGURE 4.11:- The effect of palladium additions to 3CR12 steel on the pitting potential (Ep) in 0,1N NaCl at 30°C.

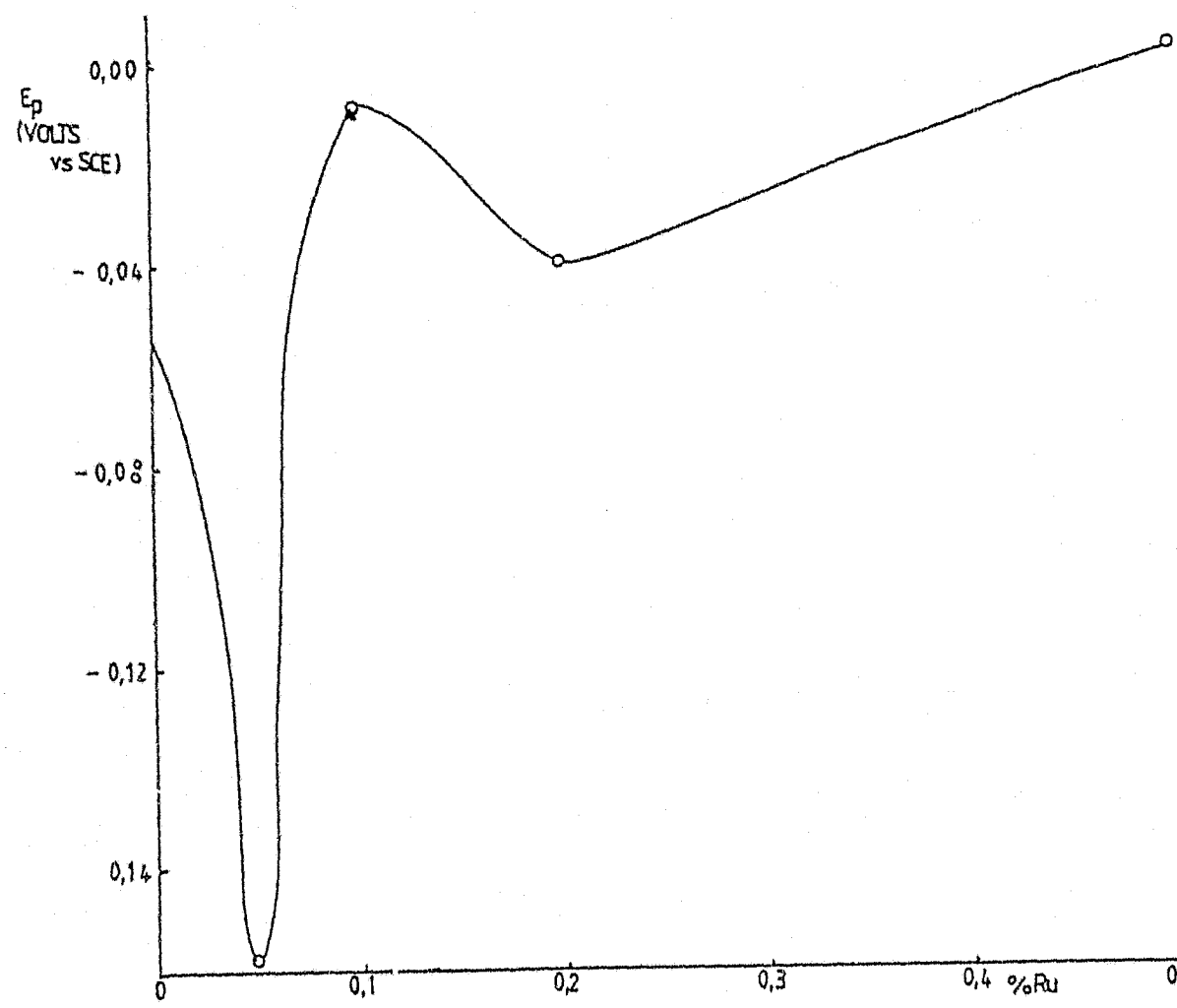

FIGURE 4.12:- The effect of ruthenium additions to 3CR12 steel on the pitting potential (Ep) in 0,1N NaCl at 30°C.

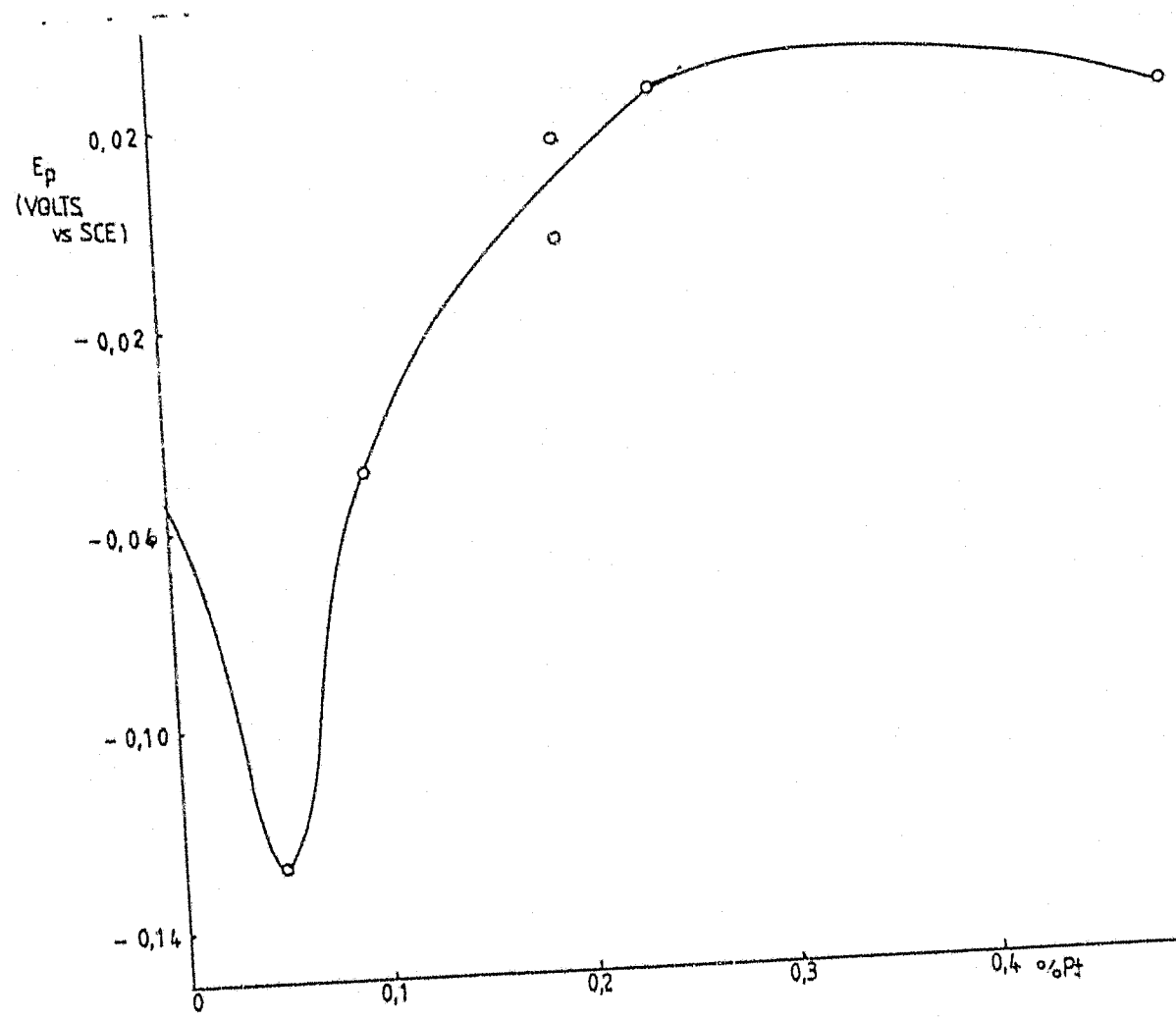

FIGURE 4.13:- The effect of platinum additions to 3CR12 steel on the pitting potential (Ep) in 0,1N NaCl at 30°C.

TABLE 4.5

PITTING RESISTANCE - POTENTIODYNAMIC TESTS

ALLOY	Ep PITTING POTENTIAL (VOLTS)	E_{prot} PROTECTION POTENTIAL (VOLTS)
D1	-0,055	-0,437
A1	-0,052	-0,371
A2	-0,024	-0,441
A3	-0,300	below E_{corr}
A4	-0,100	-0,44?
B1	-0,178	-0,422
B2	-0,009	-0,403
B3	-0,040	-0,328
B4	-0,003	-0,384
C1	-0,127	-0,476
C2	-0,051	-0,380
C3	-0,005	-0,387
C4	0,016	-0,351
C5	0,024	-0,345
C6	0,021	-0,377

TABLE 4.6

CORROSION RATES OF 3CR12-PGM ALLOYS IN 1N H_3PO_4 AT 60°C

ALLOY	CORROSION RATE OF 4 HOUR POTENTIODYNAMIC TEST, MPY	CORROSION RATE OF 240 HOUR IMMERSION TEST, MPY
H1	4,495	0,255
E1	4,940	0,227
E2	3,521	0,240
E3	4,532	0,354
E4	4,573	0,251
I1	4,057	0,367
F1	4,024	0,084
F2	5,119	0,247
F3	6,383	0,263
F4	5,566	0,293
G1	6,373	0,289
G2	6,129	0,303
G3	6,560	0,253
G4	5,993	0,311
G5	5,920	0,257

4.2.3. 1N H_3PO_4

The corrosion rates calculated via the linear resistance polarization method and the total immersion showed no significant difference (see Table 4.6). All the alloys acquired a tenacious dark oxide film on the surface which tended to inhibit corrosion. Zucchi and Trabanelli (107) are of the opinion that the salt film consists of two layers, viz the outer layer which is thicker and provides no protection, resulting from the chemical reaction of Fe^{2+} with phosphate ions and a thinner inner layer formed by the direct action of phosphate ions on iron.

4.2.4. Orange Free State Geduld Minewater

Mine waters (see Table 4.7) have been known to cause rapid corrosion of mining equipment (108-110), especially if fabricated out of mild steel. This corrosion results from the acid conditions and the ionic species present. It was thus decided to test 3CR12 in the minewater (see Table 4.8). The corrosion rates of these alloys varied considerably which is probably due to the presence of sulphate reducing bacteria (111). After cleaning the coupons it was found that crevice corrosion had taken place between the specimen and glass cradle and that only the I1 alloy showed any evidence of pitting (see Table 4.2).

TABLE 4.7

COMPOSITION OF THE ORANGE FREE STATE (GEDULD) MINEWATER

pH (at 25°C)	6,31
pH (at 21°C)	6,20
Restivity (ohm cm at 25°C)	83,6
Conductivity (mS/m)	836
Calcium Hardness (ppm as $CaCO_3$)	686
TDS	5190 ppm
pH saturation	7,9
Langlier Index	-1,7
Total Alkalinity (ppm as $CaCO_3$)	30
Chloride	3114 ppm
Fluoride	11 ppm
Nitrite	Nil ppm
Nitrate	200 ppm
Sulphate	460 ppm

TABLE 4.8

CORROSION RATE OF 3CR12-PGM ALLOYS IN ORANGE FREE STATE (GEDULD) MINEWATER

ALLOY	CORROSION RATE (mdd)
H1	0,075
E1	1,522
E2	2,232
E3	0,241
E4	1,215
I1	0,048
F1	0,012
F2	0,315
F3	0,167
F4	0,045
G1	0,031
G2	0,000
G3	0,000
G4	0,000
G5	0,105

4.2.5. Immersion Testing in Industrial Wood Pulp Liquors

The immersion coupons showed no distinctive change in their appearance after a fortnight. After 60 days immersion, some of the coupons in the green liquors (see Table 4.9) showed evidence of etching on the surface after removal of a slimey green film. There was clearly no correlation between the specimens that had been etched and those that had not, i.e. it appeared to be a random phenomena. After 180 days, the coupons in both green liquors acquired a greenish black surface film which suggests that the film could possibly be iron sulphide (112).

The immersion coupons in the weak black liquor (Ngodwana Mill) (see Table 4.9) became covered with a black film at the completion of the test. The black film was removed rather easily when scrubbed with a bristle brush. There was no significant evidence of any localised or general corrosion present on any of the 3CR12 immersion coupons. Thompson (113) used a Type 410 Stainless Steel for a suction roll in a fully martensitic condition. This 13 per cent chromium steel showed that the free ferrite, carbides and inclusions often had an influence in the areas of pitting.

In the case of the weak black liquor (Enstra Mill) (see Table 4.9), the immersion coupons did not show any change on its surface even after 180 days.

TABLE 4.9

ANALYSIS OF VARIOUS WOOD PULP LIQUORS

COMPOSITION	GL (ENSTRA)	WBL (ENSTRA)	GL (NGODWANA)	WBL (NGODWANA)
Total Solids (%)	-	6,5	-	15,1
Inorganic Content (%)	-	54,3	-	46,5
Na_2SO_3 (g/ℓNa_2O)	-	-	2	2
Na_2S (g/ℓNa_2O)	-	-	45	12
Na_2S_x (g/ℓNa_2O)	-	-	1	1
NaCl (g/ℓ) -	-	2	2	
Na_2CO_3 (g/ℓNa_2O)	108	-	68	-
NaOH (g/ℓNa_2O)	-	-	23	-
pH	12,7	12,00	12,5	11,20

4.2.5.1. Green Liquor (Enstra Mill)

The corrosion rate of 3CR12-Pd alloys increased progressively over the first 60 days, and then dropped to a lower corrosion rate for the rest of the test duration. The 3CR12-0,05Pd and 3CR12-0,1Pd alloys corroded faster than 3CR12-0,2Pd alloys, whilst the 3CR12 alloy had a consistently low corrosion rate (see Figure 4.14). The 3CR12-0,2Pd and 3CR12-0,5Pd alloys have a lower corrosion rate than the 3CR12 steel over the 180 day test duration.

The 3CR12 alloy without any additions seems to have a superior corrosion rate than the 3CR12 alloy with ruthenium additions (see Figure 4.15). After 180 days the 3CR12 alloy has a negligible corrosion rate i.e. 0,003 mpy. It should be noted that when the total immersion test reached the 120 day stage, the ruthenium additions progressively decreased the corrosion rate (see Figure 4.15).

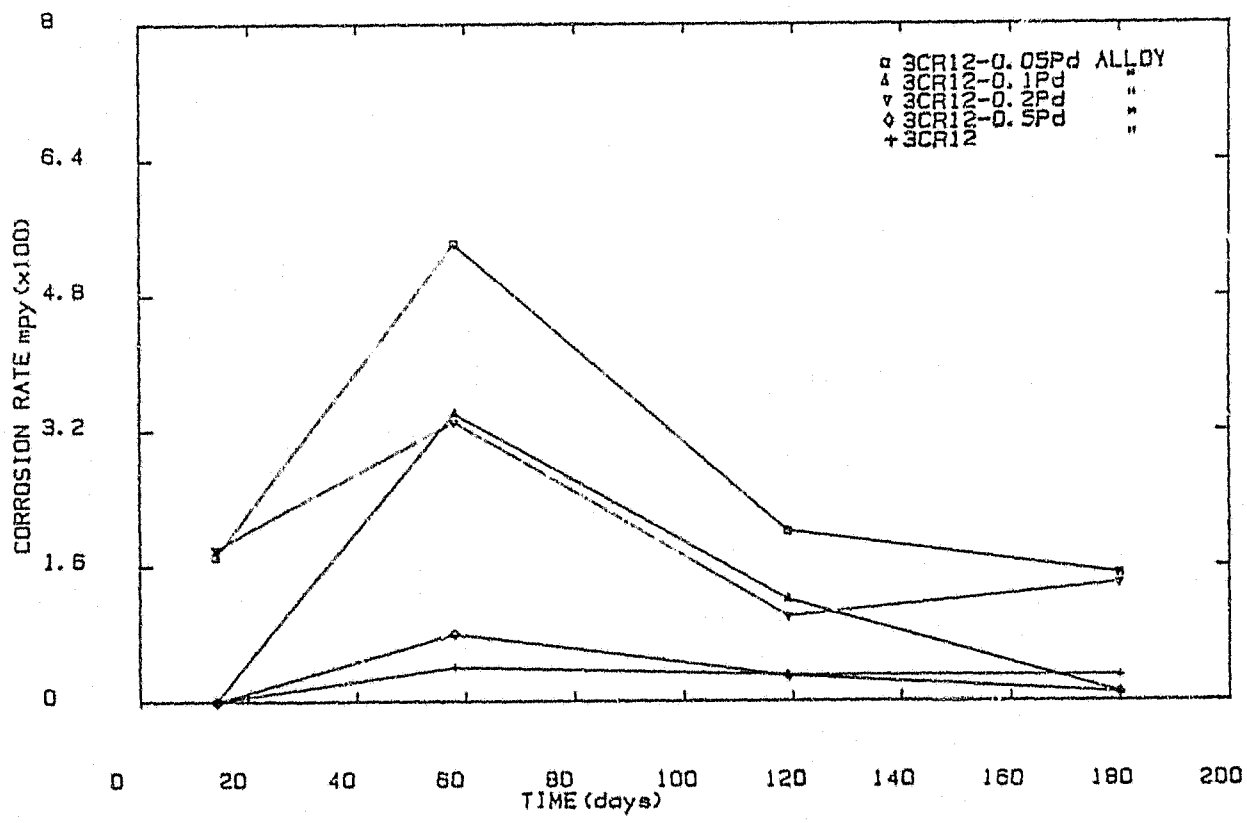

FIGURE 4.14:- The corrosion rate of the immersion coupon tested 3CR12-Pd alloys for 180 days in the green liquor (Enstra Mill) at 60°C.

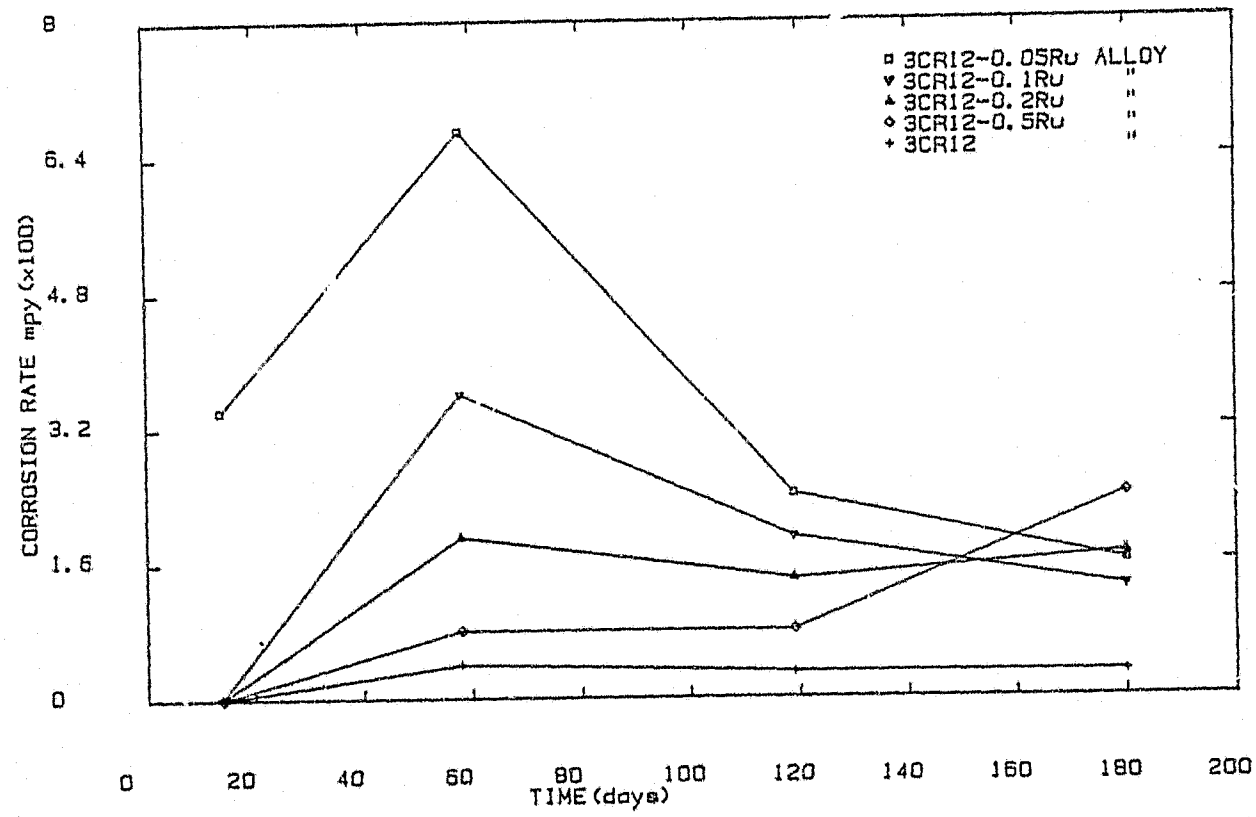

FIGURE 4.15:- The corrosion rate of the immersion coupon tested 3CR12-Ru alloys for 180 days in the green liquor (Enstra Mill) at 60°C.

The influence of 0,5% platinum addition to the 3CR12 alloy results in the highest corrosion rate over the first 60 days viz., 0,071 mpy. In fact the alloying addition seems to accelerate corrosion rather than inhibit it. The unalloyed 3CR12 steel has a better performance in terms of corrosion rate than the rest of the alloys (see Figure 4.16).

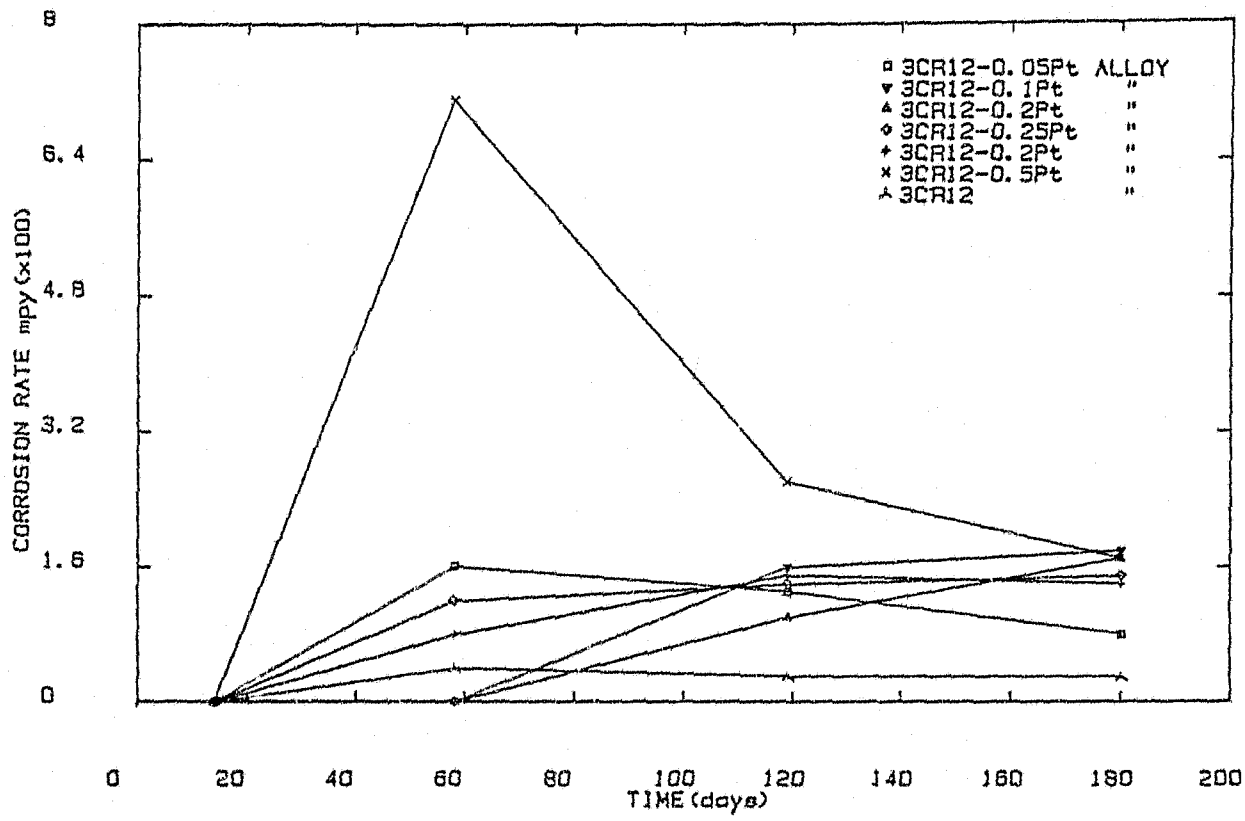

FIGURE 4.16:- The corrosion rate of the immersion coupon tested 3CR12-Pt alloys for 180 days in green liquor (Enstra Mill) at 60°C.

4.2.5.2. Weak Black Liquors (Enstra Mill)

The 0,05% palladium addition to the 3CR12 steel has little or not influence on the corrosion rate. An 0,1% palladium addition is required for effectiveness (see Figure 4.17). At a level of 0,5% palladium, the corrosion rate do not change very dramatically over the 180 day test period.

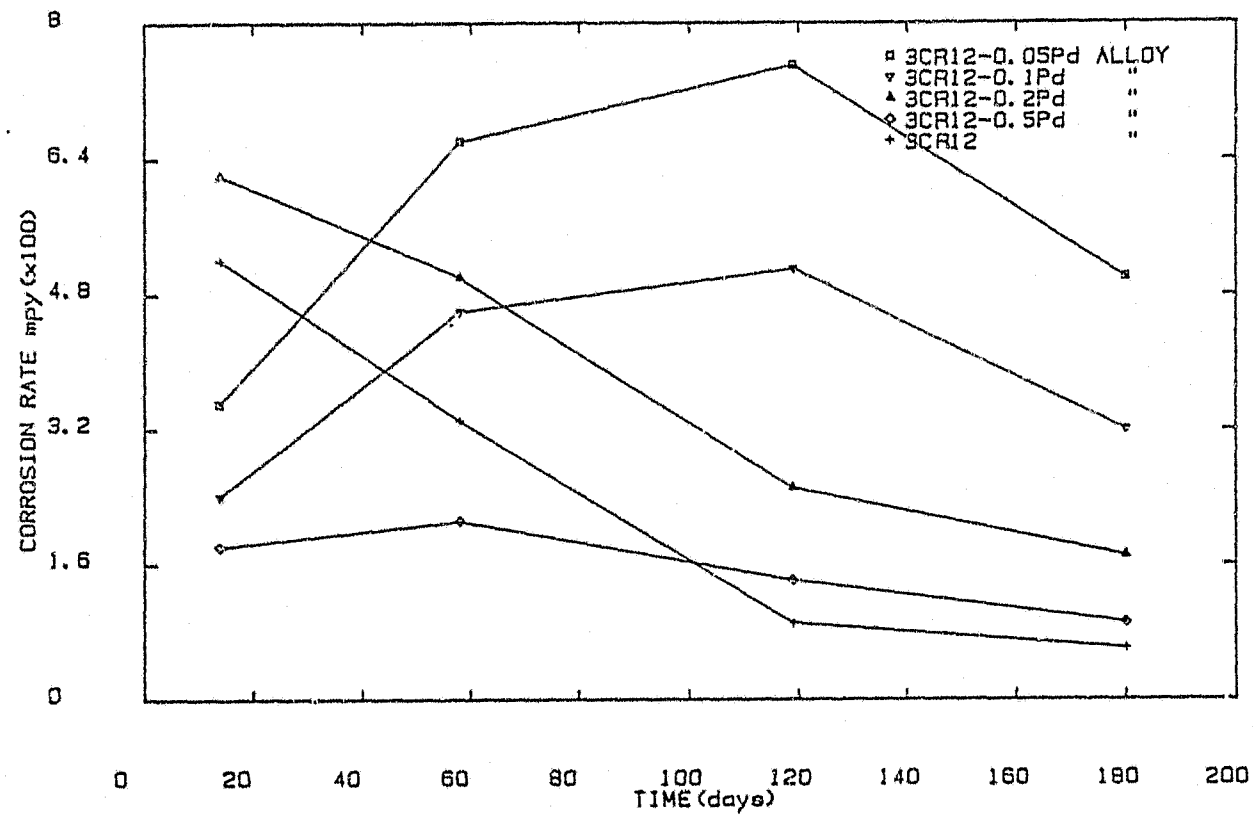

FIGURE 4.17:- The corrosion rate of the immersion coupon tested 3CR12-Pd alloys for 180 days in weak black liquor (Enstra Mill) at 60°C.

The 3CR12 steel has a higher corrosion rate compared to the 3CR12-Ru alloys after a fortnight (see Figure 4.18) viz. 0,052 mpy. At 180 days exposure the difference became negligible. On the evaluation of figure 4.18, the results show that the ruthenium additions do not contribute significantly in reducing the corrosion rate of this steel.

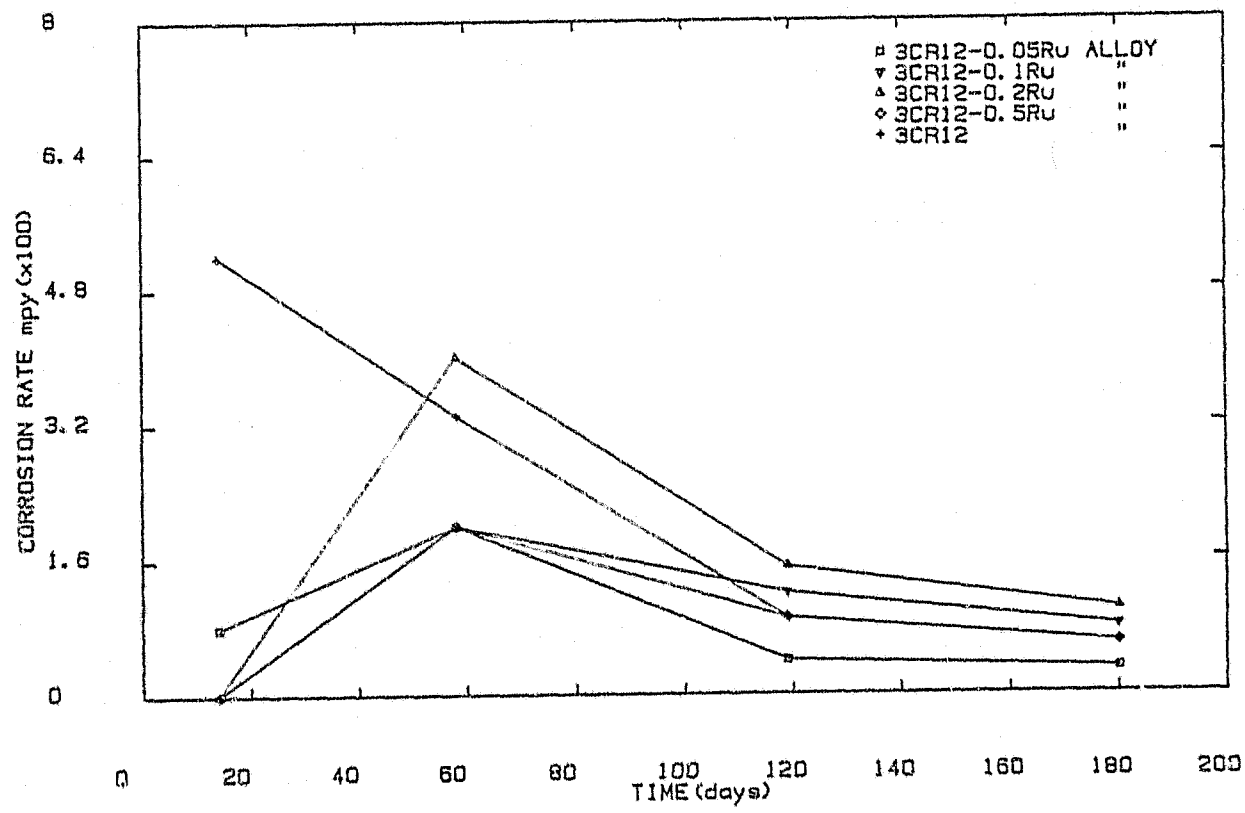

FIGURE 4.18:- The corrosion rate of the immersion coupon tested 3CR12-Ru alloys for 180 days in weak black liquor (Enstra Mill) at 60°C.

Additions of 0,05% platinum and 0,1% platinum to 3CR12 steel, do not show any significant trend in the corrosion after 180 days. However, the 0,2% platinum additions in 3CR12 steels show two different corrosion rates after 20 days (see Figure 4.19).

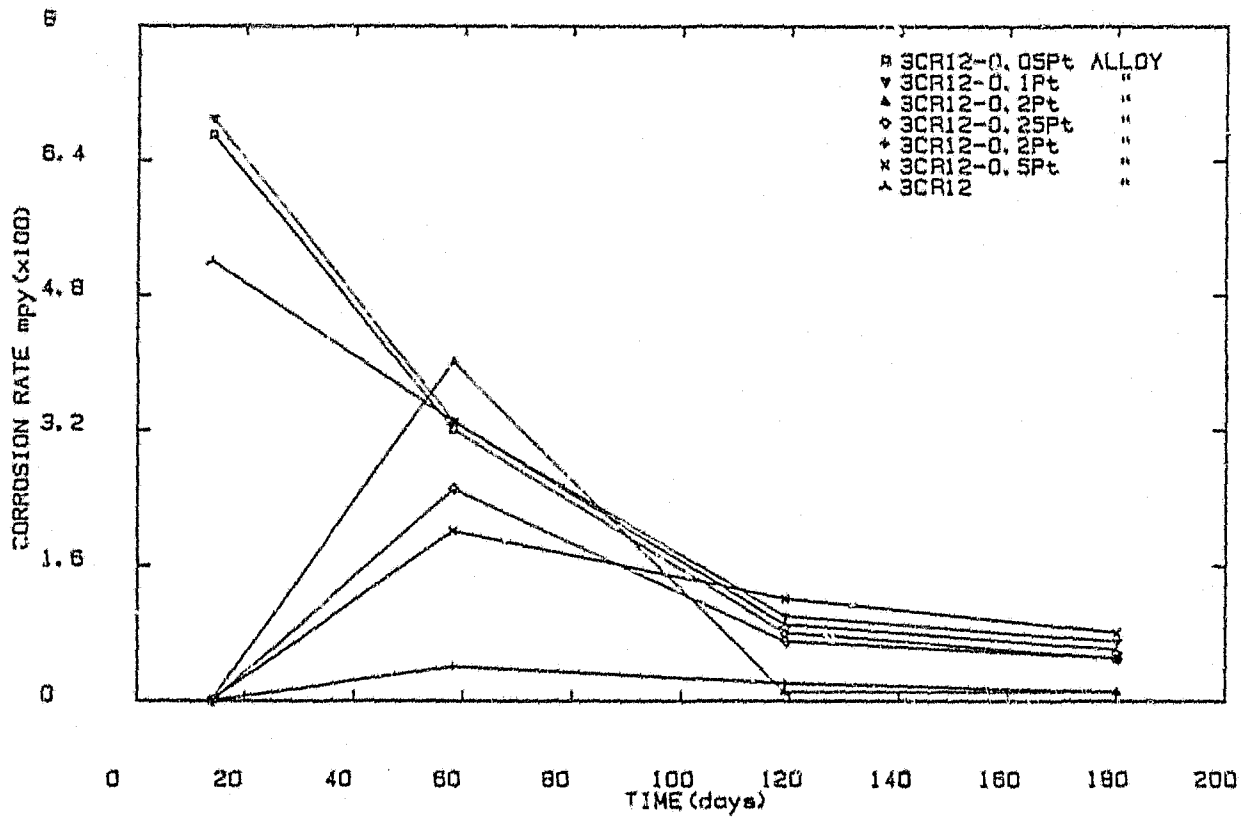

FIGURE 4.19:- The corrosion rate of the immersion coupon tested 3CR12-Pt alloys for 180 days in weak black liquor (Enstra Mill) at 60°C.

4.2.5.3. Green Liquor (Ngodwana Mill)

After 14 days, the 3CR12-0,5Pd alloy has a higher corrosion rate than the rest of the alloys. The 3CR12 steel have a better corrosion resistance than the 3CR12 steel with palladium alloying additions. On evaluating figure 4.20, one can clearly conclude that the palladium additions do not have a beneficial effect on the corrosion resistance of the 3CR12 steel. The corrosion resistance of 3CR12 steel with ruthenium additions is not improved in the green liquor (see Figure 4.21).

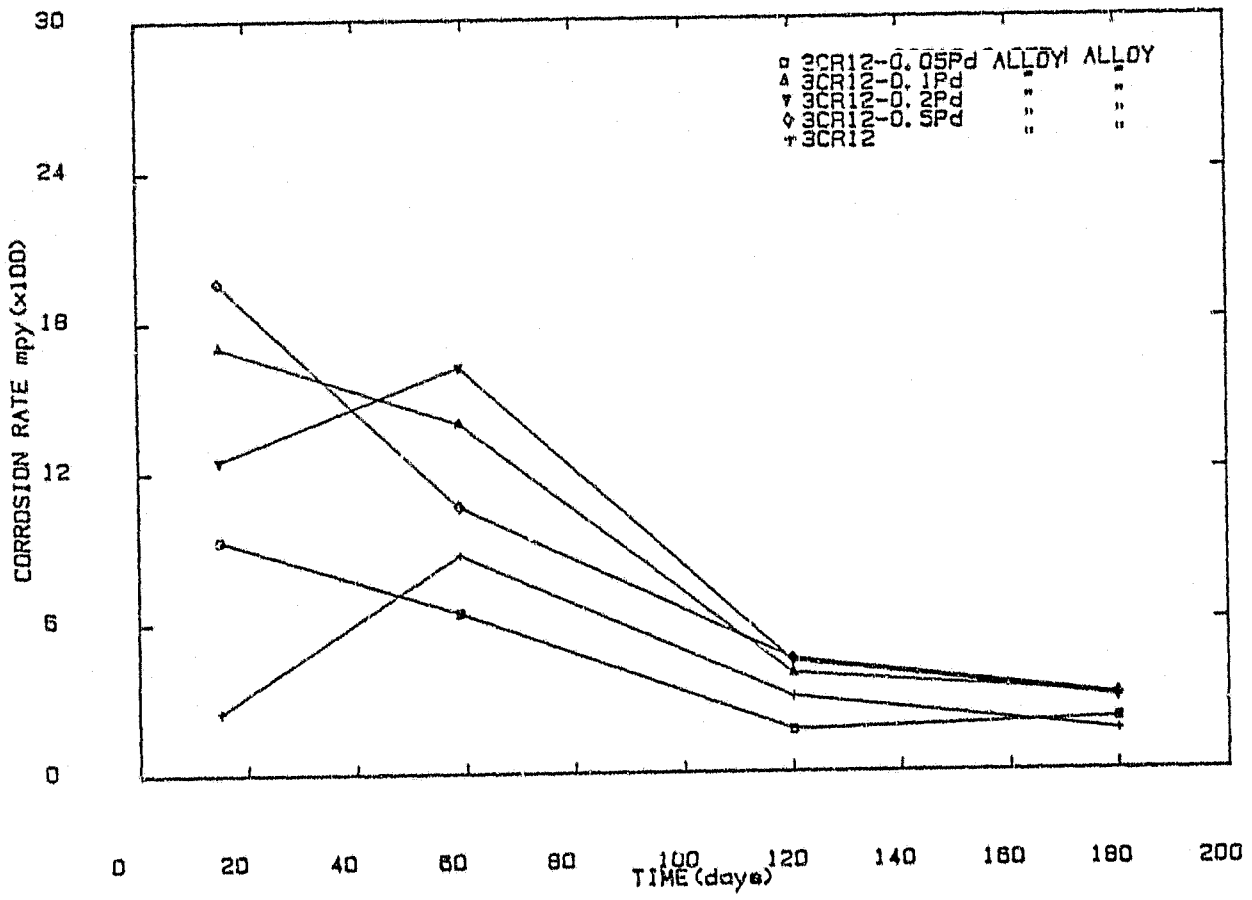

FIGURE 4..0:- The corrosion rate of the immersion coupon tested 3CR12-Pd alloys for 180 days in green liquor (Ngodwana Mill) at 60°C.

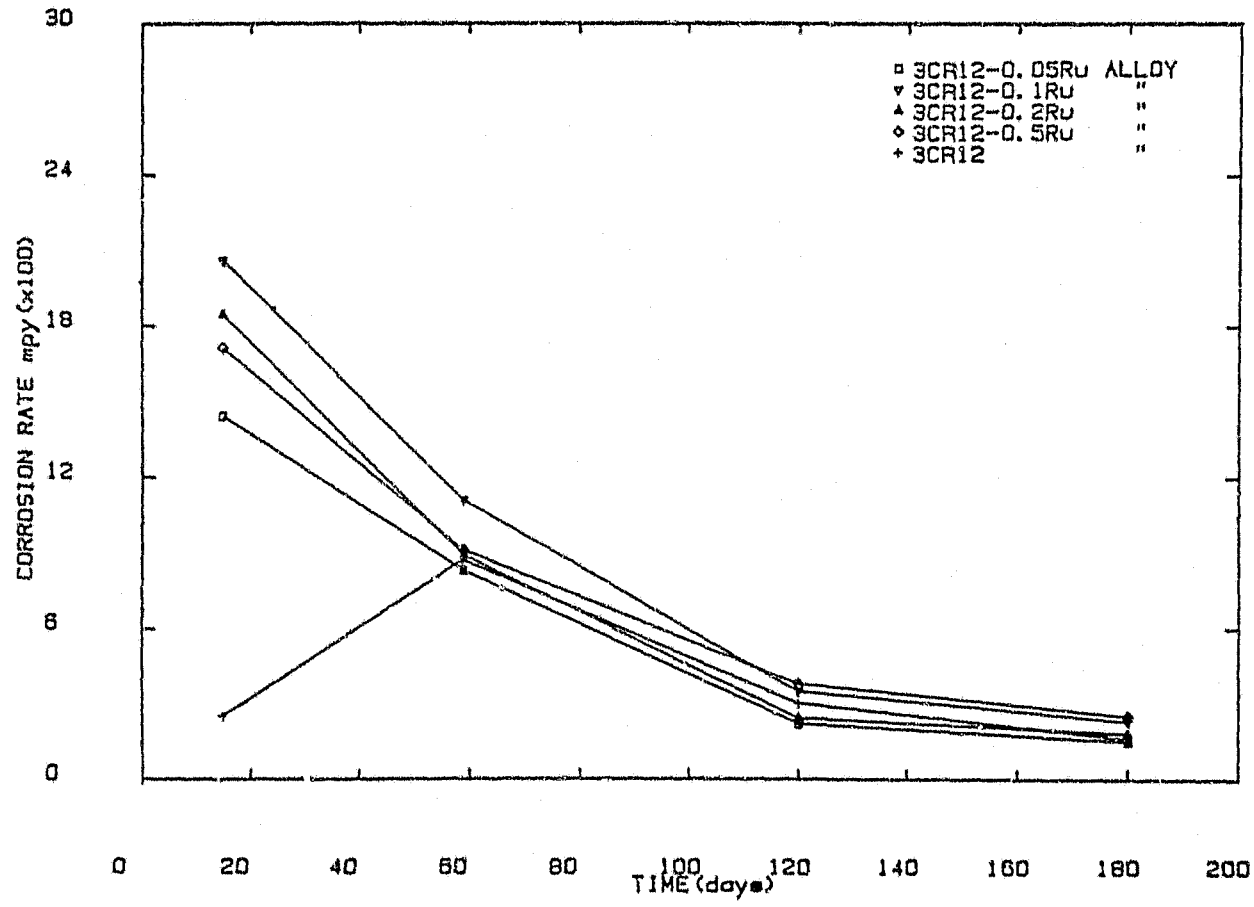

FIGURE 4.21:- The corrosion rate of the immersion coupon tested 3CR12-Ru alloys for 180 days in green liquor (Ngodwana Mill) at 60°C.

The addition of 0,5% platinum in the 3CR12 steel gives the highest corrosion rate after 14 days exposure. However, the 3CR12-0,05 Pt alloy has the highest corrosion rate after 180 days (see figure 4.22). The addition of platinum in 3CR12 steel does not show any favourable influence on the corrosion rate; in fact no stable regime is reached to conclude what addition is required for a low corrosion rate.

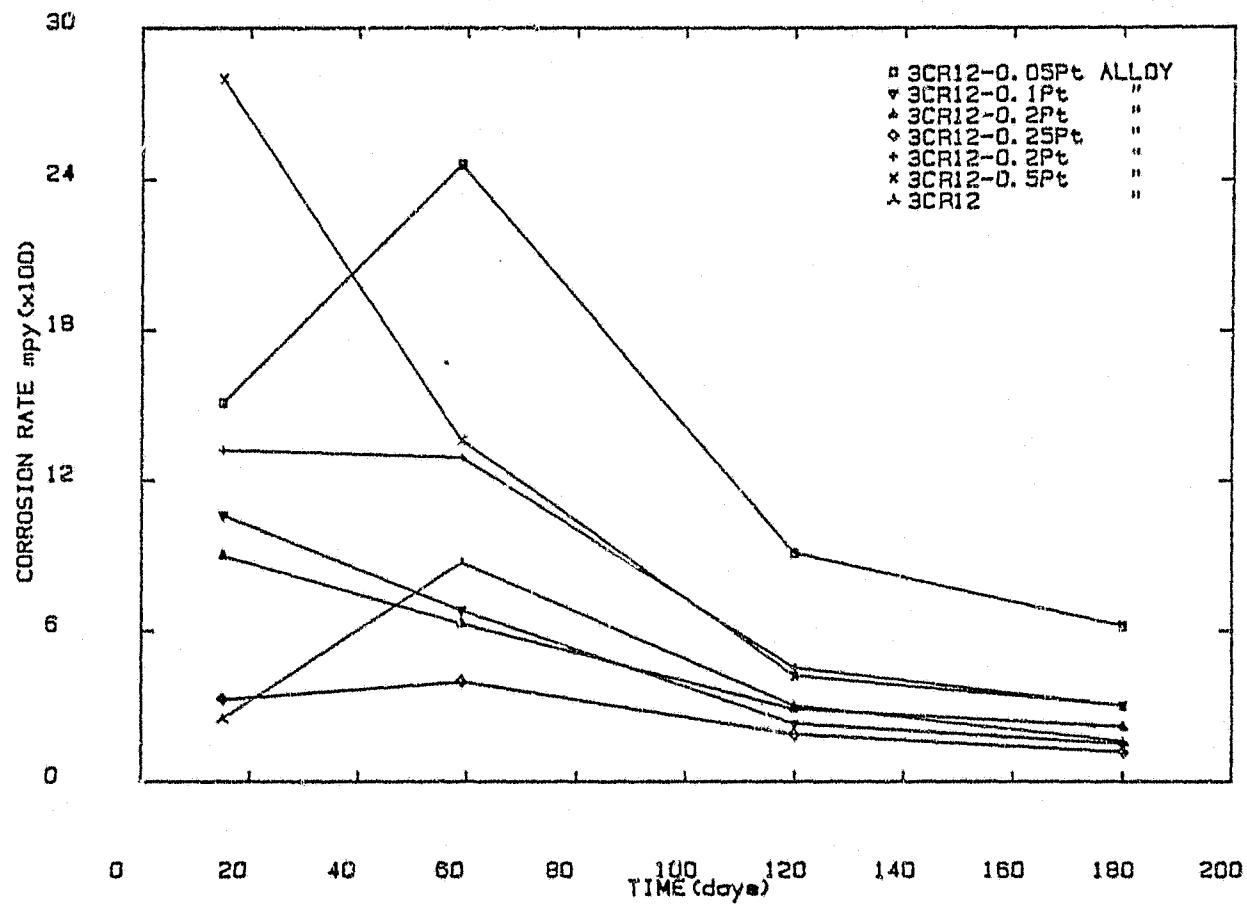

FIGURE 4.22:- The corrosion rate of the immersion coupon tested 3CR12-Pt alloys for 180 days in green liquor (Ngodwana Mill) at 60°C.

4.2.5.4. Weak Black Liquors (Ngodwana Mill)

Palladium as an alloying element in 3CR12 steel lowers the corrosion rate. 0,2% palladium give the lowest corrosion rate, whilst a 0,5% palladium addition contribute only slightly to the corrosion resistance of the steel (see figure 4.23).

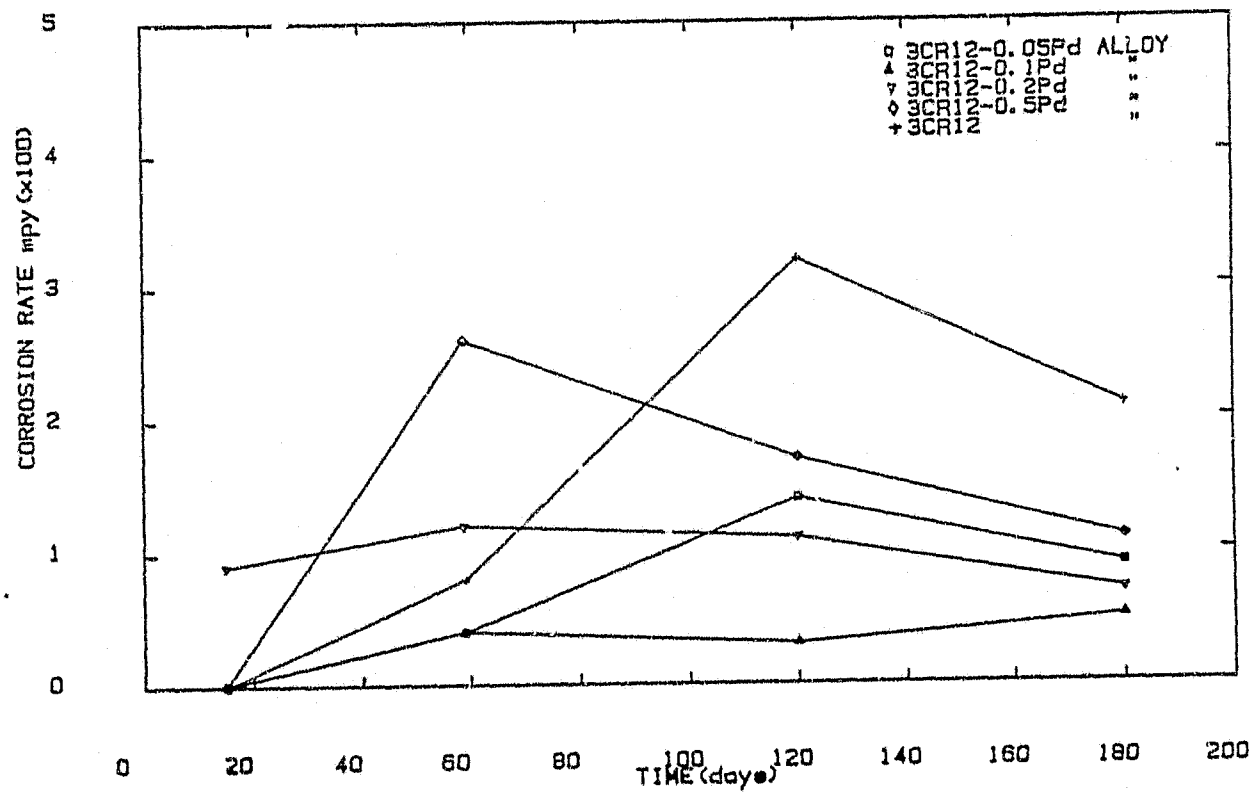

FIGURE 4.23:- The corrosion rate of the immersion coupon tested 3CR12-Pd alloys for 180 days in weak black liquor (Ngodwana Mill) at 60°C.

The 3CR12 steel has a higher corrosion rate than the rest of the alloys in this series (see figure 4.23). It can be seen that the addition of ruthenium in the 3CR12 steel is definitely beneficial. The evaluation of figure 4.24 shows that 0,1% ruthenium addition would effectively reduce the corrosion rate of the 3CR12 steel.

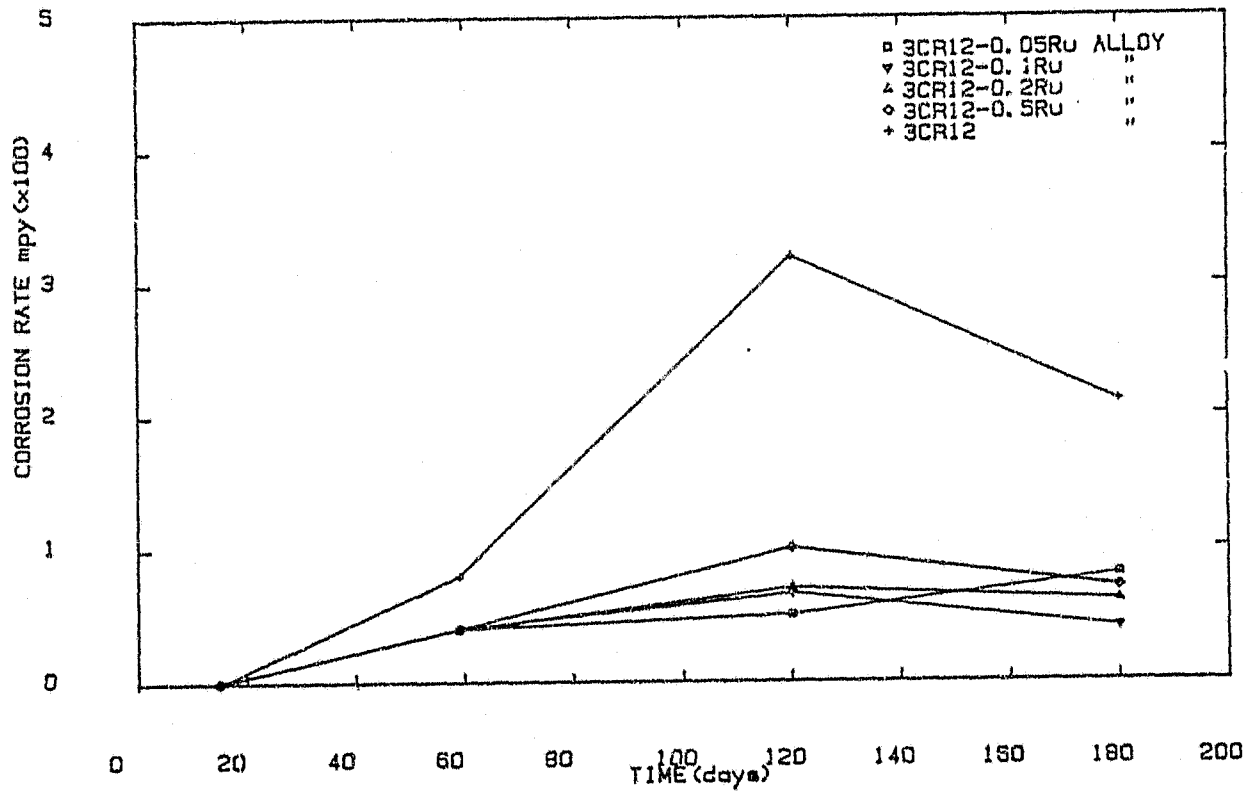

FIGURE 4.24:- The corrosion rate of the immersion coupon tested 3CR12-Ru alloys for 180 days in weak black liquor (Ngodwana Mill) at 60°C.

The 0,2% platinum addition in 3CR12 steel contributes to a low corrosion rate over the duration of the 180 day test period (see figure 4.25). The 3CR12 steel has the highest corrosion rate after the 180 day test period. Therefore the addition of platinum to the 3CR12 alloys would appear to enhance corrosion resistance.

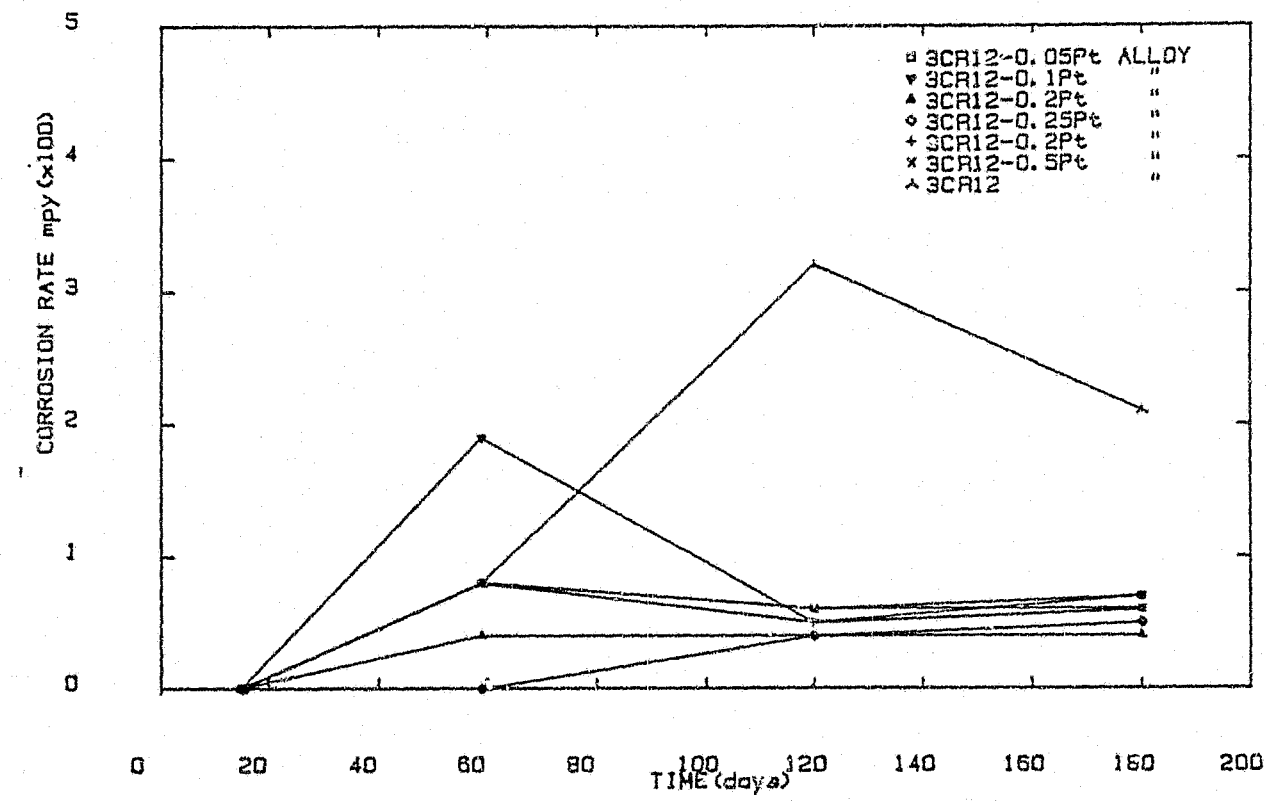

FIGURE 4.25:- The corrosion rate of the immersion coupon tested 3CR12-Pt alloys for 180 days in weak black liquor (Ngodwana Mill) at 60°C.

4.2.6. Potentiodynamic Testing in Wood Pulp Liquors

Mueller (114,115) was one of the first researchers to develop polarization curves for the study of electrochemical corrosion in the pulp and paper industry. Mueller found that the polarization curve of black liquor deviated very significantly from the curves of white liquor.

In contrast to the observations of the immersion coupons in the green liquor (Enstra Mill), the working electrodes were covered with a clear white filament, the white product is clearly a carbonate compound (see Table 4.9). Kesler (116) suggests that if the pH of the liquor is increased by adding the requisite amount of sodium carbonate then the corrosion would be reduced in the pulp and paper vessels. Teeple (117) has commented that of the two alkaline processes employed, the soda process appears to be much less corrosive to carbon steel than does the sulphate process, the Kraft process. Von Essen (118) has suggested a change to a cheap stainless steel viz., 13% chromium steel, which would overcome the problems in the sulphate pulp mills. Svendenius (119) of the Swedish Corrosion Insitute notes that green or black liquors as corrosive environments have not been specially studied so far. Tuthill (120) has extensively studied the localized corrosion of 316 Stainless Steel and 317 Stainless Steel in paper mill exposure tests.

4.2.6.1. Green Liquor (Enstra Mill)

The potentiostat was unable to give a Tafel slope extrapolation for the 3CR12 alloys because of the absence of a flat position in the curves at E_{corr}. The addition of palladium to 3CR12 steel does not contribute to a reduction in the corrosion rate according to the resistance polarization method (see Figure 4.26)

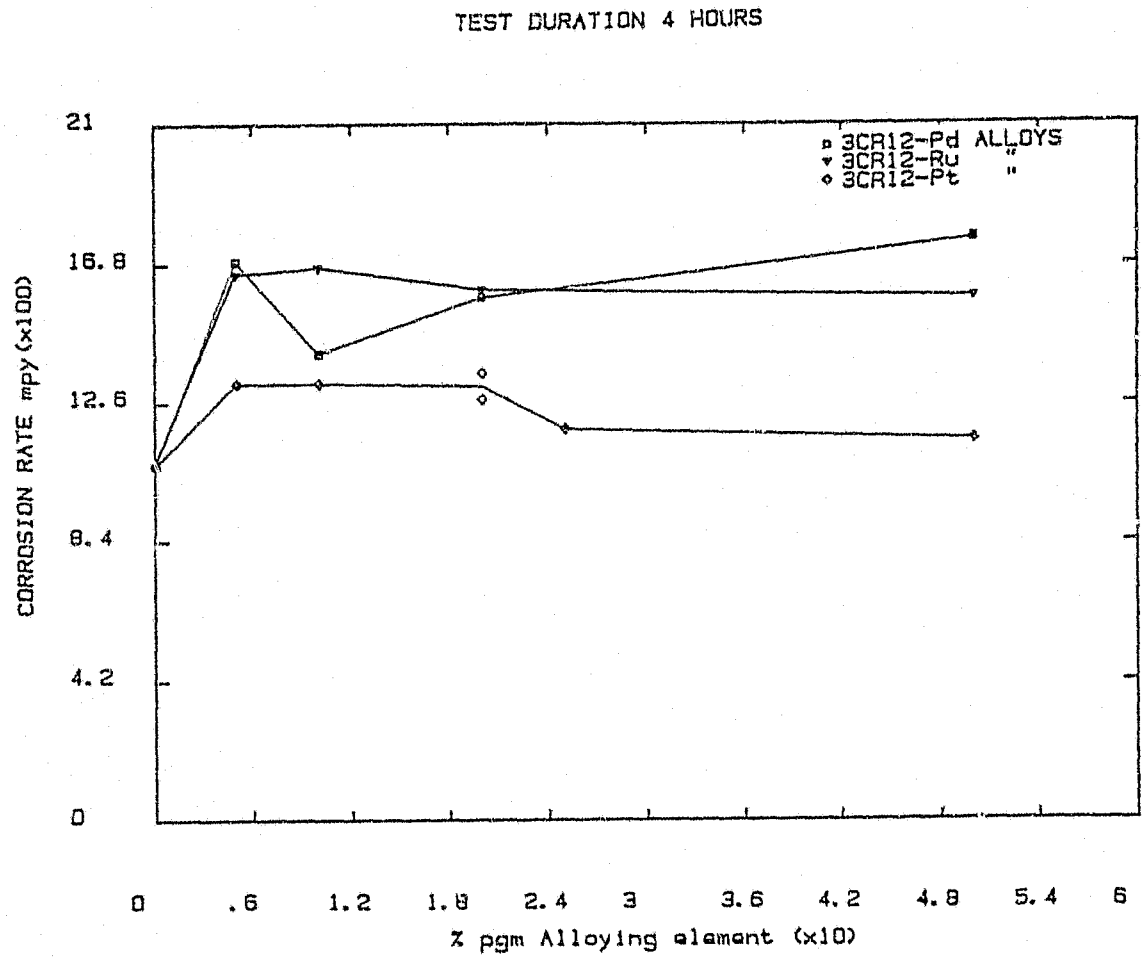

FIGURE 4.26:- The effect of platinum group metal additions on the corrosion rate of 3CR12 alloys in the green liquor (Enstra Mill) at 60°C by means of the resistance polarization.

The resistance polarization data (see Figure 4.26) shows that the 3CR12 steel is far better than the alloys with ruthenium additions. The 3CR12 steel has a corrosion rate of 0,107 mpy whilst figure 4.26 shows that 0,1% and 0,20% Pt alloying addition in 3CR12 steel increases to 0,130 mpy. 0,25% Pt and 0,50% Pt alloying addition in 3CR12 steel favours a negligible change in corrosion rate as compared to 3CR12 steel.

4.2.6.2. Weak Black Liquor (Enstra Mill)

The effect of the 0,1% Pd alloying addition in 3CR12 steel (see Figures 4.27 and 4.28) is to bring about a reduction in the corrosion rate from Tafel slope extrapolation and resistance polarization considerations. The correlation between the corrosion rate of Tafel slope extrapolation, and the resistance polarization for the 3CR12-Ru alloy appear to be very good (see Figures 4.27 and 4.28). The corrosion rates of the 3CR12-0,1 Ru and 3CR12-0,2 Ru alloy are higher than the 3CR12 steel in both the Tafel slope extrapolation and resistance polarization determinations.

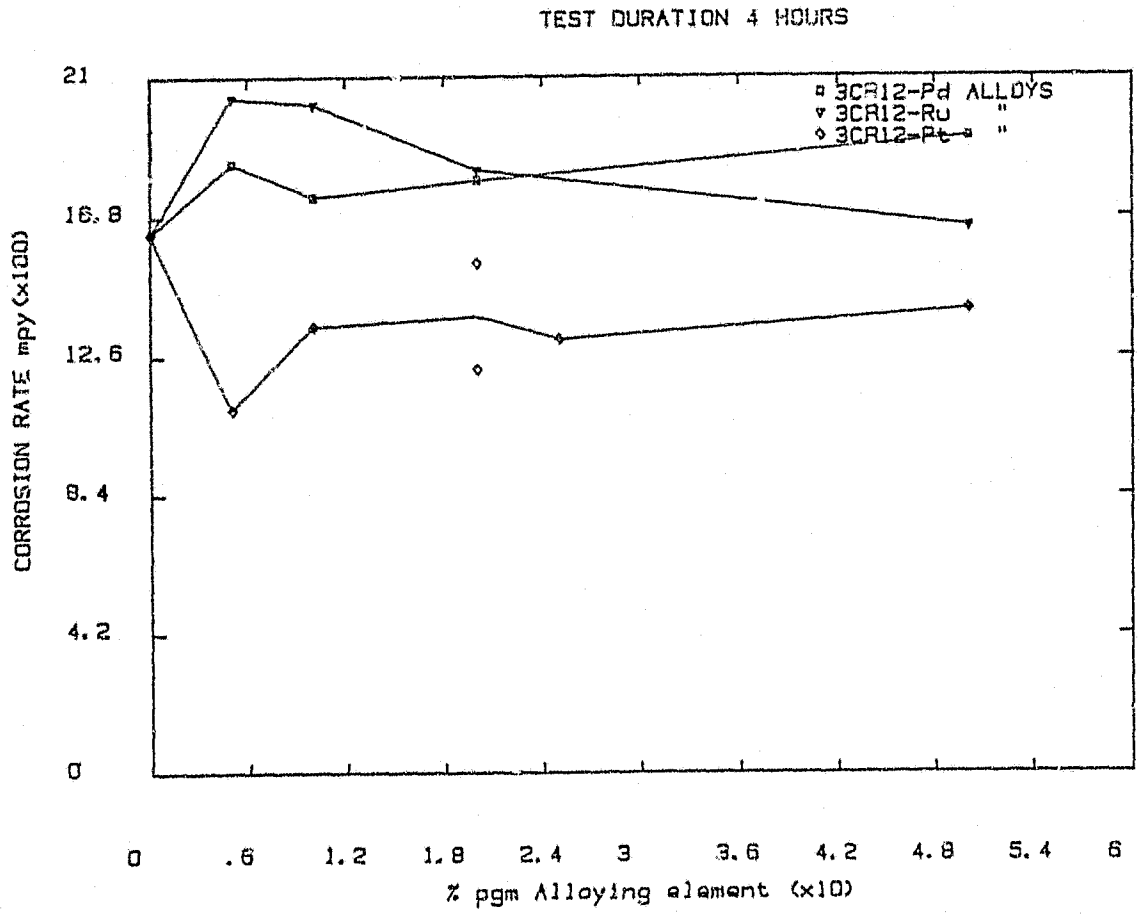

FIGURE 4.27:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the weak black liquor (Enstra Mill) at 60°C by means of the resistance polarization.

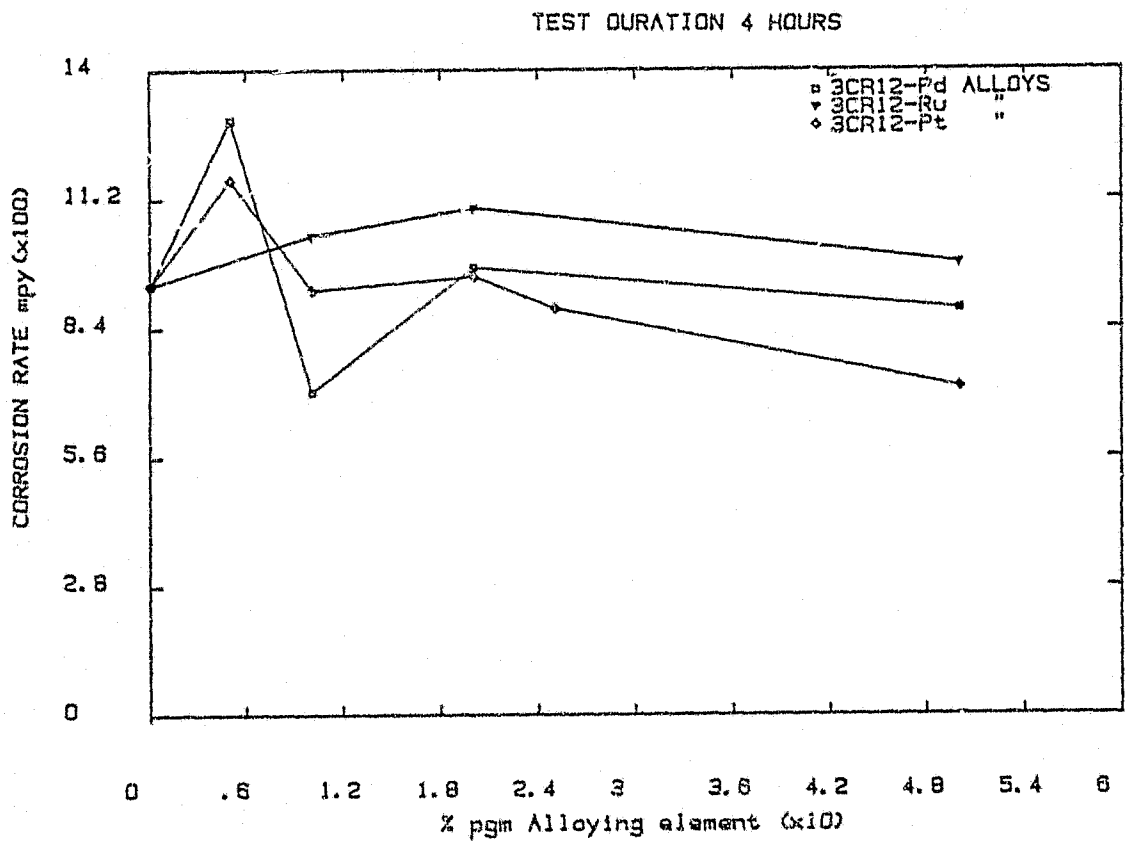

FIGURE 4.28:- The effect of the platinum group metal addition on the corrosion rate of the 3CR12 alloys in the weak black liquor (Enstra Mill) at 60°C by means of the Tafel slope extrapolation.

At levels in excess of 0,05% platinum the trend of the curves follow a similar pattern (see Figure 4.27 and 4.28). In the case of the Tafel slope extrapolation, the corrosion rate of the 0,25% and 0,5% platinum additions to the 3CR12 steel results in a slight improvement. Resistance polarization data on the other hand, suggest that the platinum addition does yield beneficial results.

4.2.6.3. Green Liquor (Ngodwana Mill)

The 0,05% palladium addition in 3CR12 steel results in a higher corrosion rate than the 3CR12 steel which can be seen from the Tafel slope extrapolation data (Figure 4.29). On the other hand, resistance polarization data (see Figure 4.30) tend to indicate that the corrosion rate of the 3CR12 steel is lower than the 0,05% palladium addition in 3CR12 steel. Otherwise the correlation of the Tafel slope extrapolation and the resistance polarization is very good (see Figure 4.29 and 4.30). 3CR12-0,2Pd steel has a better corrosion resistance than 3CR12 steel.

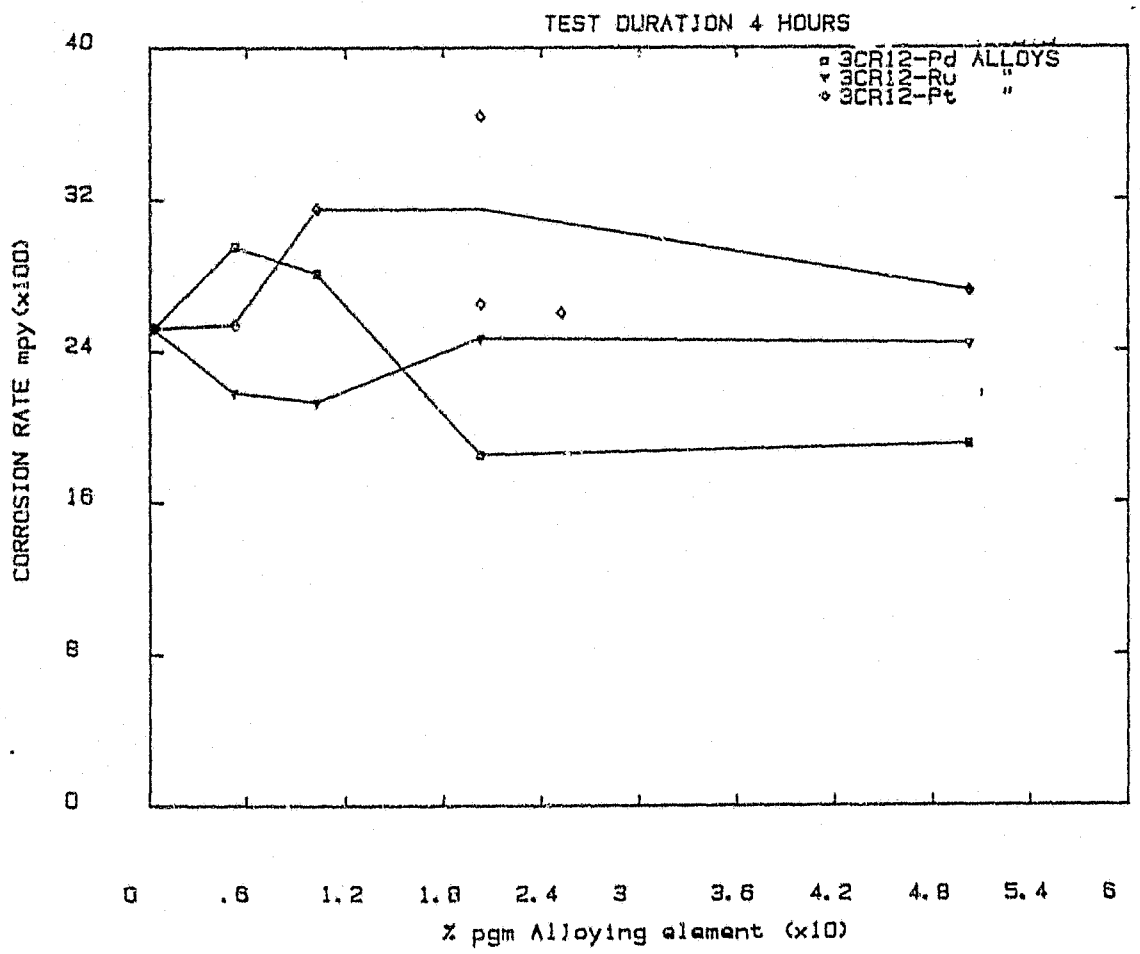

FIGURE 4.29:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the green liquor (Ngodwana Mill) at 60°C by means of Tafel slope extrapolation.

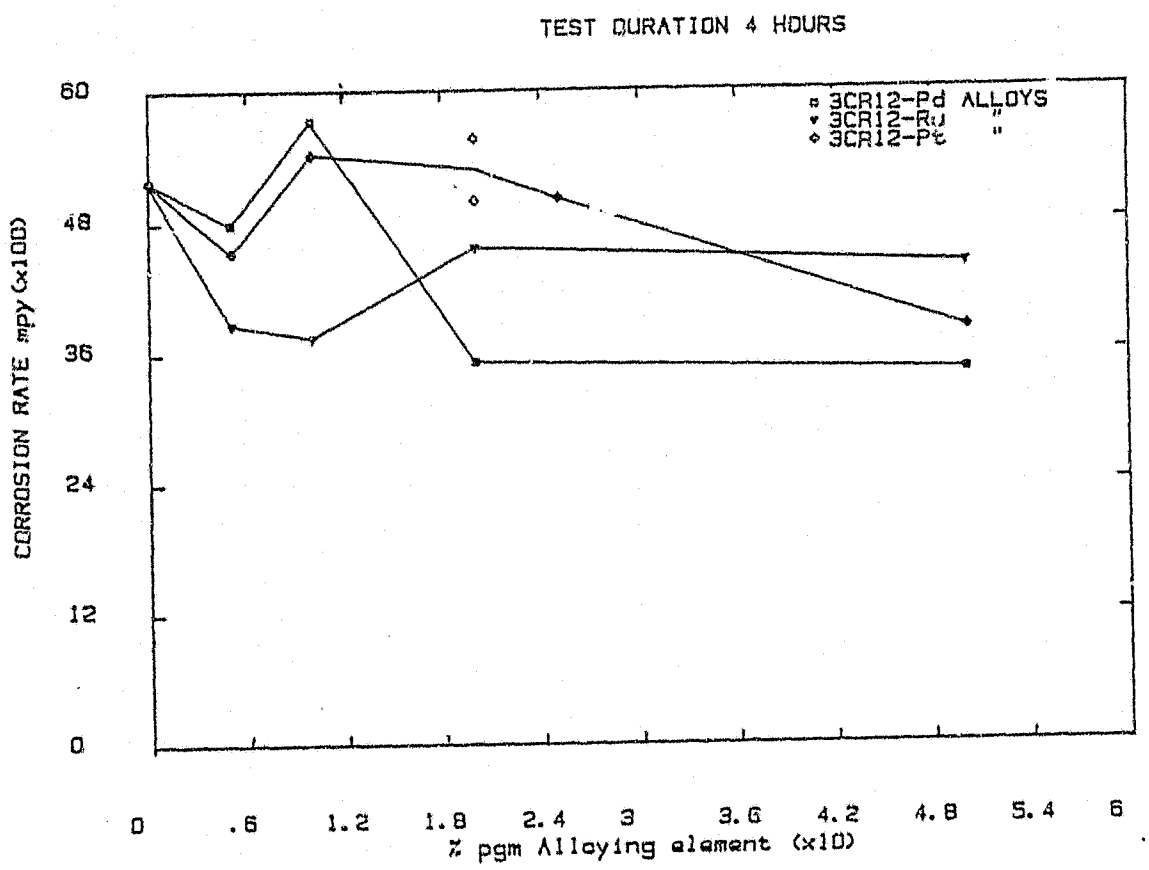

FIGURE 4.30:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the green liquor (Ngodwana Mill) at 60°C by means of the resistance polarization.

The agreement between the corrosion rates of the Tafel slope extrapolation and resistance polarization of the 3CR12-Ru alloys are very good. (See Figures 4.29 and 4.30). In fact 3CR12 steel has a higher corrosion rate than the rest of the alloys. The trend of the curves follow a similar pattern (see Figures

4.29 and 4.30) with 0,05% and 0,1% ruthenium additions in 3CR12 steel respectively having the lowest corrosion rate. However after 0,1% ruthenium addition in 3CR12 steel the corrosion rates stabilise with further additions having no influence on the corrosion rate (68).

The correlation of the Tafel slope extrapolation and the resistance polarization of 3CR12-Pt alloys is fairly good. However in the case of the Tafel slope extrapolation, the 3CR12 steel has the best corrosion resistance (see Figure 4.29). In the resistance polarization 0,5% platinum addition in 3CR12 steel has the best corrosion resistance but this is probably due to experimental error (see Figure 4.30).

4.2.6.4. WEAK BLACK LIQUOR (NGODWANA MILL)

The 0,05% palladium containing alloy has a higher corrosion rate than the 3CR12 steel in both cases (see Figure 4.31 and 4.32). As 0,5% palladium addition in 3CR12 steel could not be plotted because the Tafel slopes were not flat for extrapolation to calculate the corrosion rates. The correlation between the Tafel slope extrapolation and resistance polarization is poor.

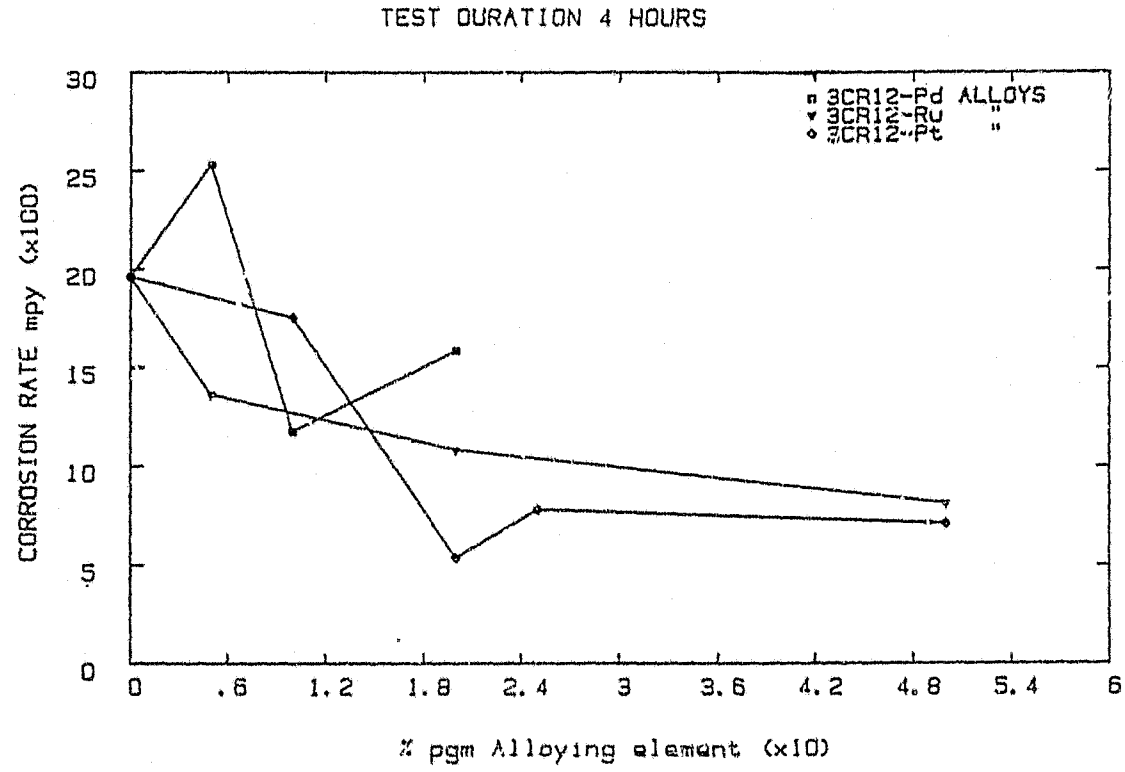

FIGURE 4.31:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the weak black liquor (Ngodwana Mill) at 60°C by means of Tafel slope extrapolation.

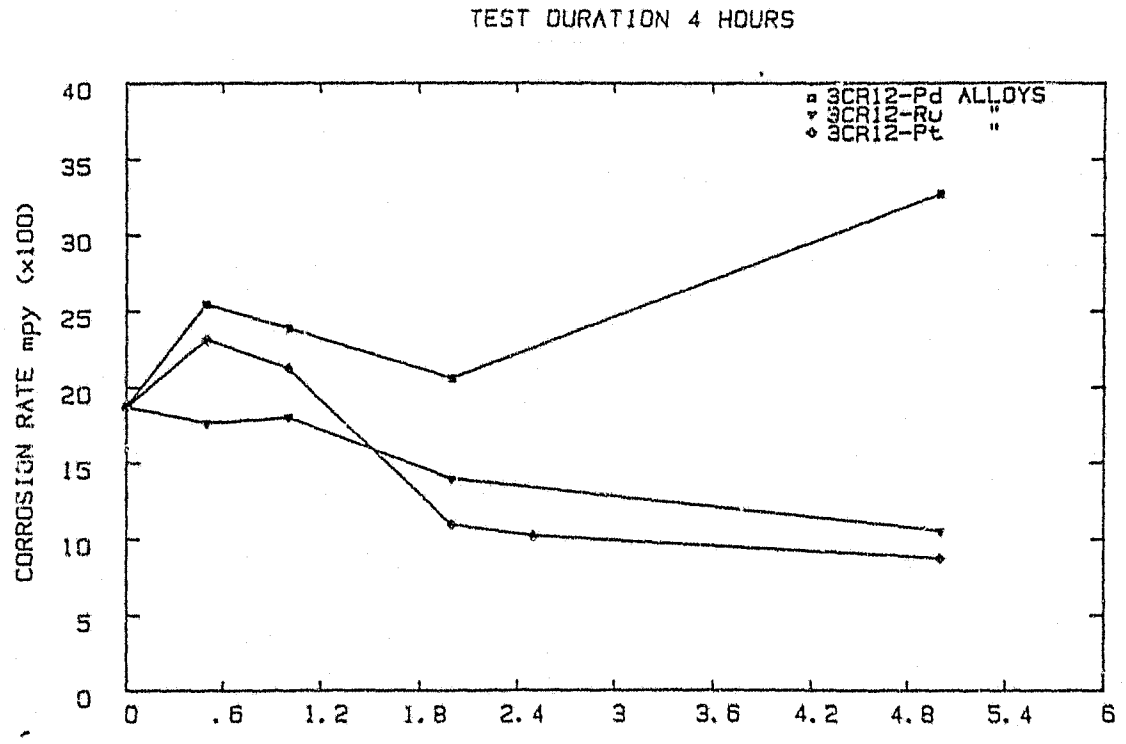

FIGURE 4.32:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the weak black liquor (Ngodwana Mill) at 60°C by means of the resistance polarization.

The 3CR12 steel has a higher corrosion rate than the 3CR12-Ru alloys. The drop in corrosion rate follows a similar trend in both cases, viz., Tafel slope extrapolation and resistance polarization methods (see Figure 4.31 and 4.32). The 0,5% ruthenium containing alloy has a corrosion rate of 0,081 mpy, which is the lowest in the case of Tafel slope extrapolation (see Figure 4.31). However, this is in agreement with the resistance polarization data (see Figure 4.32) in which 3CR12-0,5Ru alloy has a corrosion rate of 0,105 mpy.

3CR12 steel has a relatively poor corrosion resistance when compared 3CR12-Pt alloys. The corrosion rates of the Tafel slope extrapolation and the resistance polarization correlated fairly well (see Figure 4.31 and 4.32). The 0,25% platinum addition in 3CR12 steel has the best corrosion resistance (see Figure 4.32).

4.2.7. Total Immersion Test versus Potentiodynamic Test

The correlation of the corrosion rate between the immersion coupons and the resistance polarization of the 3CR12-Pd alloys in Figures 4.26 and 4.33 do not appear very well. This could be due to the presence of the black film formed on the surface of the immersion coupons resulting in a significant decrease in the corrosion rate of the 3CR12-0,2Pd alloy. The comparison between the trend of the total immersion specimens and the potentiodynamic test, of the 3CR12-Ru alloy is very good (see figures 4.26 and 4.33). The 3CR12-0,2Ru alloy provides the best corrosion resistance in the green liquor (Enstra Mill). The effect of the platinum additions to 3CR12 immersion coupons do not appear to correlate well with the potentiodynamic tests (see Figures 4.26 and 4.33).

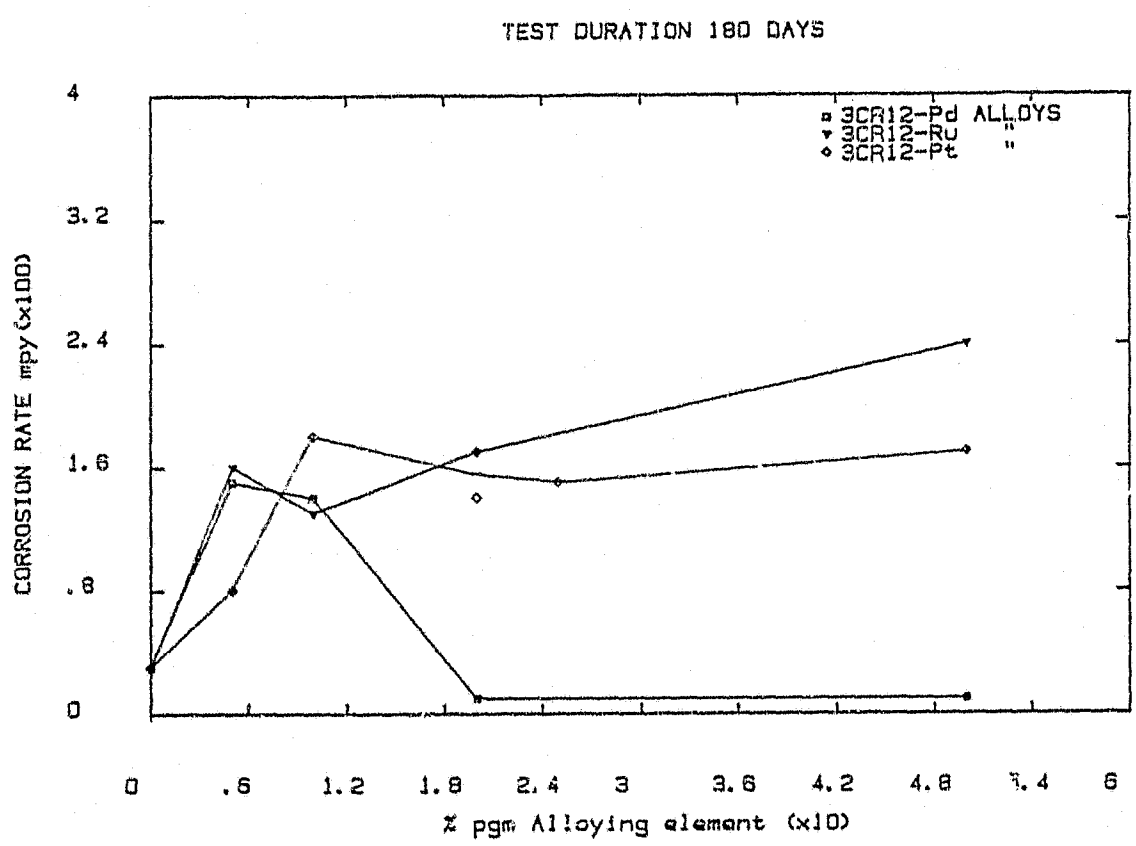

FIGURE 4.33:- The effect of platinum group metal additions on the corrosion rate of the 3CR12 alloys in the green liquor (Enstra Mill) at 60°C.

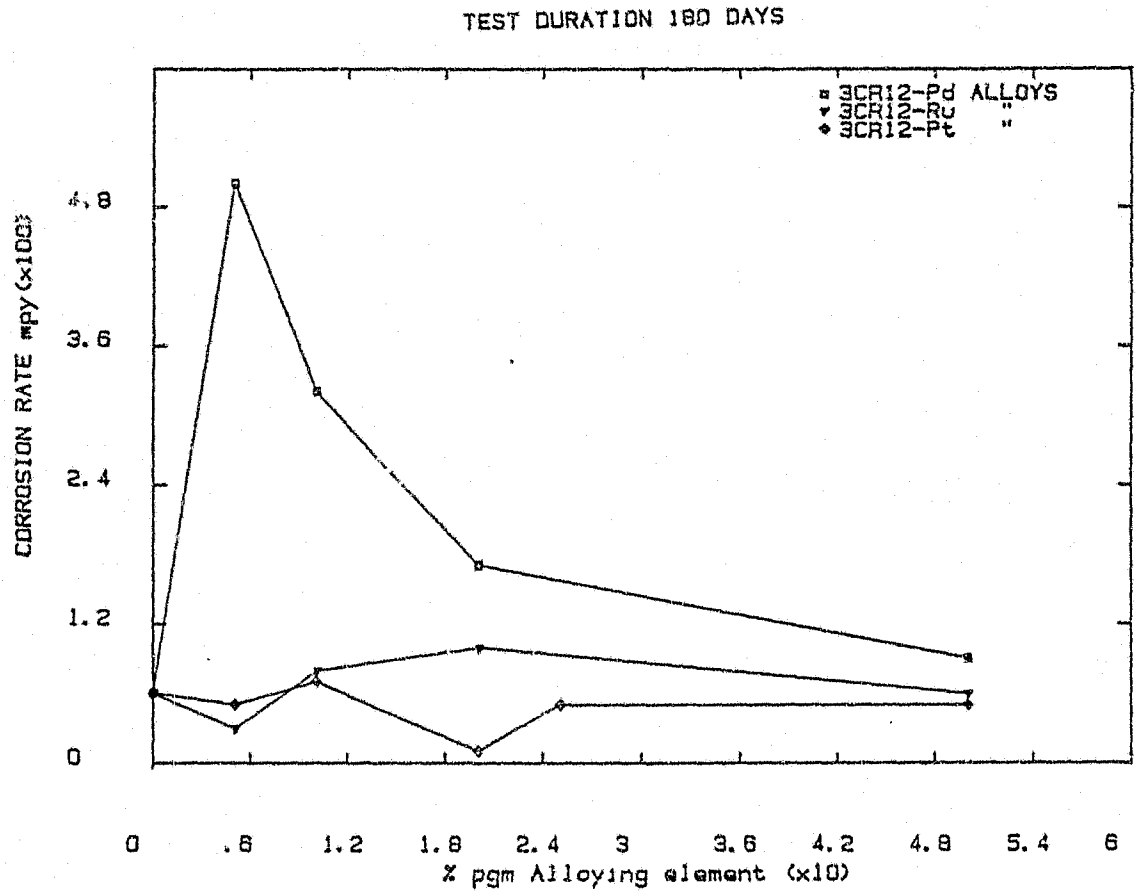

FIGURE 4.34:- The effect of platinum group metal additions on the corrosion rate of the 3CR12 alloys in the weak black liquor (Enstra Mill) at 60°C

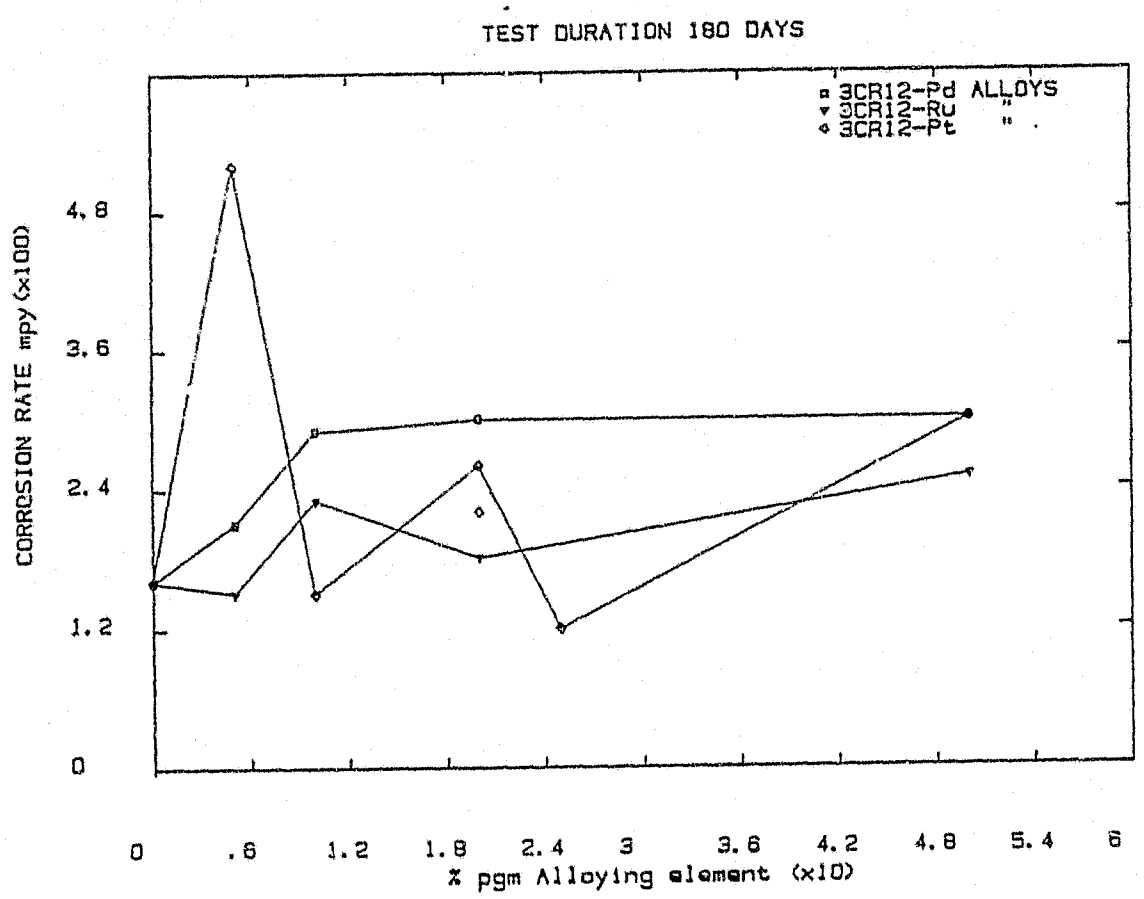

FIGURE 4.35:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the green liquor (Ngodwana Mill) at 60°C.

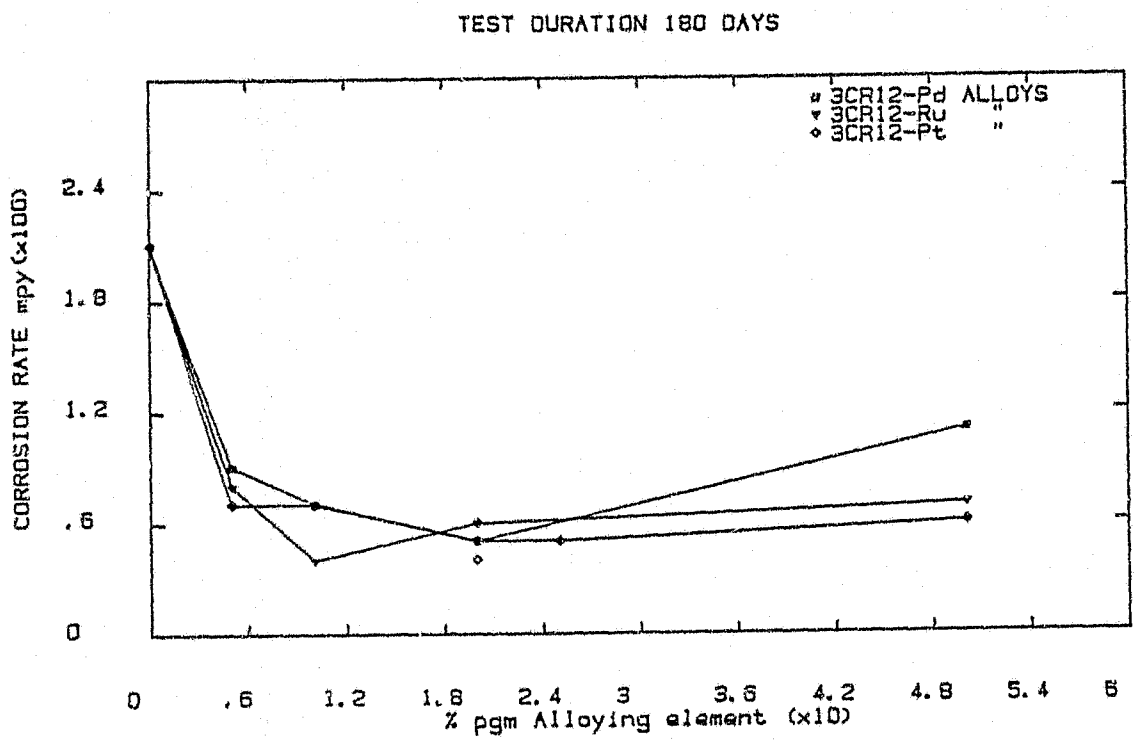

FIGURE 4.36:- The effect of the platinum group metal additions on the corrosion rate of the 3CR12 alloys in the weak black liquor (Ngodwana Mill) at 60°C.

For the immersion coupons, the 3CR12-Pd alloys have a higher corrosion rate in the weak black liquors (Enstra Mill) (see Figure 4.34) whilst in the resistance polarization tests shows that the palladium addition in 3CR12 alloy has no beneficial effect (see Figure 4.27). The Tafel extrapolation results are

in contradistinction to these resistance polarization results (see Figures 4.27 and 4.28). The correlation between the total immersion tests and potentiodynamic tests for the ruthenium addition 3CR12 steel appear to be in good agreement (see Figure 4.27, 4.28 and 4.34). Platinum additions in 3CR12 steel are beneficial in both the long term test and the short term test (see Figures 4.31, 4.32 and 4.33).

From a comparison for Figures 4.29, 4.30 and 4.35 for the 3CR12-Pd alloys conflicting results are obtained in the immersion and the potentiodynamic tests. This is also the case for the other two series of alloys, 3CR12-Ru and 3CR12-Pt alloys (see Figures 4.29, 4.30 and 4.35). The corrosion test results for the three series of alloys in the weak black liquor (Ngodwana Mill) are in good agreement in both the immersion and potentiodynamic tests (see Figures 4.31, 4.32 and 4.36). The 3CR12-Ru and 3CR12-Pt alloys appear to be better than the 3CR12 steel.

5. CONCLUSIONS

1. The impact property values of the 3CR12-Ru alloys were more reproducible than the 3CR12-Pt alloys.

2. The fractographs of 3CR12-Pd and 3CR-Ru alloys showed evidence of delaminations which are characteristic of 3CR12.

3. The 3CR12-Pd and 3CR12-Ru alloys had fracture surfaces which revealed both characteristic ductile and brittle features simultaneously.

4. When the amounts of pgm's alloying additions were increased, they cathodically polarized the 3CR12 alloy which correspondingly shifted the corrosion potential of the 3CR12 alloy in the noble direction. The platinum and ruthenium alloying additions seemed to have more pronounced effect on the corrosion potential of 3CR12.

5. The primary passivation potential of the three series of alloys in 1N H_2SO_4 at 30°C are shifted in the noble direction, whilst the critical current density for passivity especially for the ruthenium and platinum additions to 3CR12 steel respectively, is shifted to a lower minimum current density.

6. The passive range of the alloys was generally speaking constant.

7. The potentiodynamic and total immersion test in 1N H_2SO_4 at 30°C show that the 3CR12-0,2 Ru alloy and 3CR12-0,25Pt alloy have the best corrosion resistance. This result is confirmation that a certain minimum amount of pgm alloying addition is required to improve the corrosion resistance of stainless-type alloys.

8. The pitting susceptibility of 3CR12-Ru alloys and 3CR12-Pt alloys decreases after 0,1% pgm alloying compared to 3CR12-Pd alloys.

9. The alloys tested did not show any significant difference as regards to corrosion resistance in 1N phosphoric acid and in O.F.S. Mine Water.

10. A straight 3CR12 steel immersed in the green liquor for 180 days was found to have superior corrosion resistance to those alloys containing pgm alloying additions.

11. On the other hand, 3CR12 alloys with pgm additions, immersion tested in weak black liquor for 180 days show better corrosion resistance than 3CR12 steel.

12. The correlation between the corrosion rate of the total immersion tests and potentiodynamic tests in woodpulp liquors are in good agreement, with a few exceptions. The 3CR12-Ru and 3CR12-Pt alloys in the woodpulp liquors have a good correlation between the corrosion rate of the total immersion tests, and the potentiodynamic tests.

13. Electrochemical corrosion rate measurements in woodpulp liquors are considered inconsistent. No reliable data could be obtained when comparing the Tafel slope extrapolation and resistance polarization methods.

9. The alloys tested did not show any significant difference as regards to corrosion resistance in 1N phosphoric acid and in O.F.S. Mine Water.

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13. Electrochemical corrosion rate measurements in woodpulp liquors are considered inconsistent. No reliable data could be obtained when comparing the Tafel slope extrapolation and resistance polarization methods.

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