Effect of Additions of Ru and Pd on the Electrochemical Behaviour of Austenitic Stainless Steel in Organic Acids

J.H.Potgieter[1,2], J.Thomson[3], F.V.Adams[4], A.S.Afolabi[5,]*

[1]School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, Wits, 2050, South Africa
[2]Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa
[3]Division of Chemistry and Environmental Science, School of Science and the Environment, Manchester Metropolitan University, Oxford Road, M1 5GD, Manchester, United Kingdom
[4]Department of Petroleum Chemistry, School of Arts and Sciences, American University of Nigeria, PMB 2250, Yola, Adamawa State, Nigeria
[5]Department of Civil and Chemical Engineering, College of Science, Engineering and Technology, University of South Africa, P/Bag X6, Florida 1710, Johannesburg, South Africa
[*]E-mail: afolaas@unisa.ac.za

This study investigated the influence of the additions of various amounts of ruthenium (Ru) and palladium (Pd) on the electrochemical behaviour and corrosion resistance of 304 stainless steel in a number of different organic acid media, by measuring their electrochemical polarization behaviour in these media at room temperature. The analysis of the results obtained showed that the alloyed sample containing almost equal amounts of Pd and Ru (PdRu) exhibited more corrosion resistance in all the organic acids studied compared to the rest of the other samples. It was observed that the PdRu alloy sample was most susceptible to corrosion in lactic acid and least in citric acid. All the Ru alloyed samples (Ru1, Ru2 and Ru3) corroded less in lactic acid medium and more in oxalic acid (Ru1 and Ru2) and citric acid (Ru3). It can be confirmed that the addition of Pd and Ru in the alloyed samples considerably improved the corrosion resistance of these alloys.

1. INTRODUCTION

The increasing applications of stainless steels in most of the major industries, especially in the nuclear, power, marine, food production, chemical and electrochemical, medical and petroleum

industries, have made them versatile construction materials. This is mainly due to their high corrosion resistance, high strength and toughness [1–3]. The 304 type stainless steel is probably the most versatile and most widely used of all stainless steels. Its chemical composition, mechanical properties, weldability and corrosion/oxidation resistance provide the best all-round performance at relatively low cost. It also has excellent low temperature properties and can be hardened by cold working. The non-magnetic properties, combined with exceptionally high toughness at all temperatures, make this steel an excellent choice for a wide variety of applications in chemical plants, industrial and maritime fields [4]. As a result of this, many investigations are continually being carried out on this steel on a regular basis [5–9].

Organic acids are weak acids and do not dissociate completely in water, as do the strong mineral acids. Lower molecular mass organic acids such as formic and lactic acids are miscible in water, but higher molecular mass organic acids, such as benzoic acid, are insoluble in molecular (neutral) form. On the other hand, most organic acids are very soluble in organic solvents. Organic acids such as formic or acetic acids are used for oil and gas well stimulation treatments, at high temperatures or when long contact times between acid and pipe are needed. Citric and oxalic acids are used for rust removal, to dissolve iron oxides without damaging the base metal. Organic acids are also used in food preservation because they can penetrate the cells of certain pH-sensitive bacteria and disrupt their normal physiology. Lactic acid (and its salts: sodium lactate and potassium lactate) are widely used as antimicrobial agents in food products, in particular, meat and poultry products, such as ham and sausages [10]. The various applications of stainless steel, especially in oil production, transportation, and food production, are accompanied by their interaction with some of these organic acids, particularly acetic acid which is the most abundant in oil wells [11–12].

The resistance of stainless steel depends, among many other factors, on its passive nature, alloy chemistry and the specific environment to which it is exposed. The inert nature of the passive film on the surface is dependent on its stability in the medium of exposure [3, 13–14]. A good strategy to improve corrosion resistance is by carefully monitoring the alloying contents in the steel. PGMs are known for their resistance to oxidation and corrosion due to their high activation energy. Thus, studies have shown that the corrosion resistance of some stainless steels can be improved by alloying them with small additions of PGMs [15–18]. This approach to improving the corrosion resistance of a base alloy by adding a small amount of a PGM to it, is known as cathodic modification [19]. However, most of these investigations had been conducted in inorganic acids [16, 20–23].

Furthermore, only a few investigations had been carried out on the corrosion behaviour of stainless steels in organic acids [24–29]. However, no evidence could be found in the literature that such cathodically modified stainless steels have been investigated in organic acids. Most recent studies of alloys containing PGMs [19,30] have concentrated on Ru additions, and little evidence could be found in the recent literature on the effect of palladium on the corrosion behaviour of stainless steels metal in organic acid media [12]. This study therefore investigates the effect of addition of small quantities of ruthenium and palladium additions and their possible synergistic effect on the corrosion and electrochemical properties of a 304-type stainless steel in selected organic acid media.

As stainless steels are often used in environments containing organic acids, such as in the petrochemical process and food industries, it is important to improve their corrosion resistance. The

findings of this study suggests that it can be done by adding small amounts of PGMs either alone or in combination to a commonly used stainless steel alloys. It therefore makes a new and useful contribution about the corrosion prevention of these materials in various organic acids media and potential new areas of application thereof.

2. MATERIALS AND METHOD

The stainless steel samples used in this study were 304-type austenitic stainless steel containing various amounts of ruthenium and palladium. The chemical compositions of these samples as supplied by the manufacturer are shown in Table 1 [31–32].

Table 1. Percentage chemical compositions of stainless steel samples

Percentage chemical composition					
Sample	Fe	Cr	Ni	Pd	Ru
304	68.64	19.01	9.4	0	0
Ru1	67.49	18.68	9.54	0	0.13
Ru2	67.98	18.88	9.57	0	0.26
Ru3	68.32	18.39	9.41	<0.01	1.01
Pd3	67.53	18.29	9.39	0.96	<0.01
PdRu	69.06	18.49	9.52	0.13	0.14

Samples of these stainless steel alloys were prepared for electrochemical analysis. They were prepared by attaching a copper wire to one side of each metal sample and mounting it in resin. The surfaces of the samples were ground with silicon carbide paper from 180 down to 1200 grade (corresponding to size 15.3 μm), washed with distilled water, degreased in acetone to remove any particles that might have remained on the surfaces after polishing, and finally dried in air.

The electrochemical and corrosion behaviour of these samples were investigated using potentiodynamic polarization measurements in 1.0 molar solutions of acetic, lactic, citric, and oxalic acids. The electrochemical cell used was a conventional three − electrode cell comprising the sample as the working electrode, the saturated calomel electrode (SCE) immersed in 3.0 M KCl salt bridge, and graphite counter electrode. All electrochemical measurements were made at room temperature (about $20\pm3^{o}C$) with a Princeton potentiostat/galvanostat (Model 273A computer controlled) using the general purpose electrochemical software (Powercorr suite). The software determined the corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion current density (i_{corr}) from the polarization experiments, and calculated the corrosion rates. Working electrodes were immersed in the electrolytes and allowed to stabilized at the open circuit potential (OCP) for 5400 seconds (90 minutes) before

measuring the potentiodynamic polarization in accordance with the ASTM standards (ASTM, 1992). The polarization curves were measured at a scan rate of 0.2 mV/s and the potential versus the current density of each samples were recorded. The electrolytes were replaced after each scan while the samples were repolished after each experiment.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour of alloys

3.1.1. Potentiodynamic polarisation of alloys in acetic acid medium
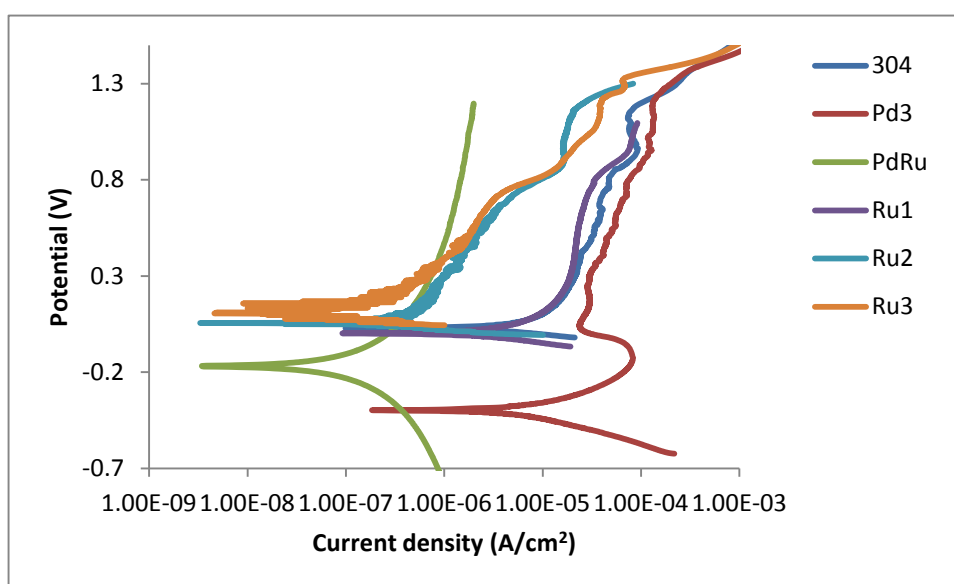
Figure 1. Potentiodynamic scans of the various alloy samples in acetic acid

Table 2. Polarization data obtained for the alloy samples in acetic acid

Corrosion media	Alloy type	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	βa (V/dec)	$-\beta c$ (V/dec)	Corrosion rate (mm/yr)
Acetic acid	304	0.0285	0.0990	0.0381	0.0103	0.0901
	Pd3	-0.3978	0.1840	0.0801	0.0637	0.1001
	PdRu	-0.1713	0.0036	0.0279	0.0957	0.0007
	Ru1	0.0018	0.0920	0.0119	0.0043	0.0729
	Ru2	0.0555	0.0033	0.0243	0.0270	0.0054
	Ru3	0.1055	0.0046	0.0358	0.0756	0.0022

The potentiodynamic polarization tests for the 304 stainless steel and its alloys were investigated in 1 M acetic acid in order to study their corrosion current, passivity and the effect of Pd, Ru and their combined effect on the corrosion behaviour of 304 alloys. The Table 2 shows the E_{corr}, I_{corr}, tafel slopes and corrosion rates obtained. The results show that the samples alloyed with the combination of Pd and Ru exhibits the highest corrosion resistance in acetic acid. The corrosion potential of the samples alloyed with Ru moved to more positive potentials with an increase in Ru added to the alloy. This correlates with an observation made by Olaseinde et al. [33] on the effect of 0.15 % Ru addition on the electrochemical studies of Fe-21Cr-

1Ni duplex stainless steels at various temperatures in 1 M sulphuric acids. These alloys (304 alloyed with Ru) showed a decrease in corrosion current density from 0.0920 $\mu A/cm^2$ to 0.0033 $\mu A/cm^2$ with an increase in Ru additions. Consequently, the corrosion rate of Ru alloyed samples decreased with increase in Ru addition. The sample containing only Pd shows the least corrosion resistance, a characteristic that is also revealed in the corrosion potential, corrosion rate and corrosion current density parameters of this alloy. Thus, the corrosion resistance of the alloys tested in acetic acid are in the order PdRu>Ru3>Ru2>Ru1>304>Pd3.

In direct reduction of organic acids, acid is usually reduced at the metal surface in addition to the reduction of hydrogen ions which is typical for all acids. When a metal corrodes, the rate at which it corrodes is generally controlled by the cathodic reaction. The cathodic and anodic reactions of metals in organic acid have been proposed by several authors [34-35] and more distinctive explanation was given in a review by Abd El–Maksoud [36]. Reactions 1, 2 and 3 give the cathodic and anodic reaction of metal in organic acid (acetic acid) [37].

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{1}$$
$$2HAc + 2e^- \rightleftharpoons H_{2(g)} + 2Ac^-_{(aq)} \tag{2}$$

The anodic reaction which occurs at the surface of the metal in order to balance the charge is the dissolution of iron:

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \tag{3}$$

3.1.2 Potentiodynamic polarisation of alloys in citric acid medium

The results of the potentiodynamic polarization measurements which were carried out to determine the corrosion rates and to evaluate the passivity behaviour of 304 alloys in citric acid are presented in Figure 2. The E_{corr}, I_{corr}, tafel slopes and corrosion rates obtained from the measurements are given in Table 3. It is clear that only one sample (Ru3) shows a distinct active to passive transition behaviour during polarization from active to more noble potentials. The rest of the alloys including 304 displayed mostly pseudo-passivity behaviour in this medium.
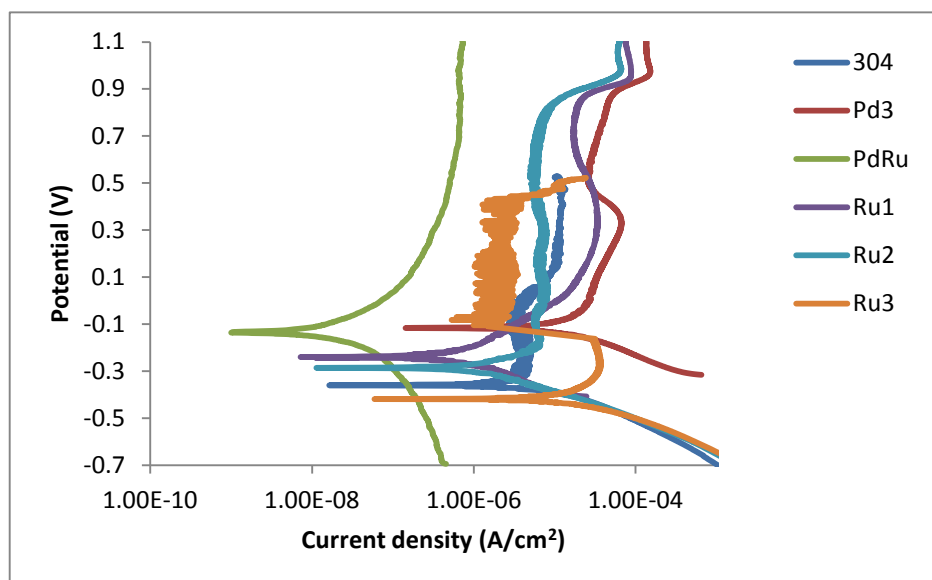
Figure 2. Potentiodynamic scans of the various alloy samples in citric acid

The sample alloyed with Pd exhibited a more noble corrosion potential than all the other samples. However, this sample shows the highest corrosion current density, which resulted in an increased corrosion rate. Contrary to the observation made in acetic acid, the corrosion potential, corrosion current density and corrosion rate of samples alloyed with Ru increased with an increase in the amount of Ru alloyed to the 304 alloy. This behaviour has been observed previously in inorganic mineral acids also, i.e. that when too little Ru is present to improve the corrosion resistance, increasing amounts increased the corrosion rate [15]. The alloy containing the combination of Pd and Ru again showed better corrosion resistance than the rest of the alloys with individual amounts of Pd and Ru. The corrosion resistance of the alloys studied in citric acid is in the order PdRu>Ru1>Ru2>304> Ru3 ~ Pd3.

Table 3. Polarization data obtained for the alloy samples in citric acid

Corrosion medium	Alloy type	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	βa (V/dec)	$-\beta c$ (V/dec)	Corrosion rate (mm/yr)
Citric acid	304	-0.3605	0.0163	0.07151	0.5156	0.0467
	Pd3	-0.1170	0.1430	0.0154	0.0361	0.1389
	PdRu	-0.1365	0.0010	0.0199	0.0544	0.0001
	Ru1	-0.2403	0.0072	0.0438	0.2106	0.0095
	Ru2	-0.2863	0.0113	0.0544	0.3116	0.0212
	Ru3	-0.4193	0.0590	0.0850	0.6132	0.1698

3.1.3 Potentiodynamic polarisation of alloys in lactic acid medium

Figure 3 shows the polarization curves of 304 alloyed samples studied in 1 M lactic acid. The sample alloyed with the lowest amount of Ru showed a marginally more positive corrosion potential

than the alloy with 0.3% Ru, and the corrosion current density values decrease with increasing higher amounts of Ru. Meanwhile, the alloy containing only Pd produced the highest corrosion rate and corrosion current density compared with all the other alloys. These results indicate that the addition of Ru in the 304 alloy resulted in better corrosion resistance compared to Pd. Ru's better corrosion improvement in comparison with that of Pd is also a known observation in inorganic mineral acids [19]. Only the base 304 alloy displays typical active to passive transition behaviour, while the rest display pseudo passivation.
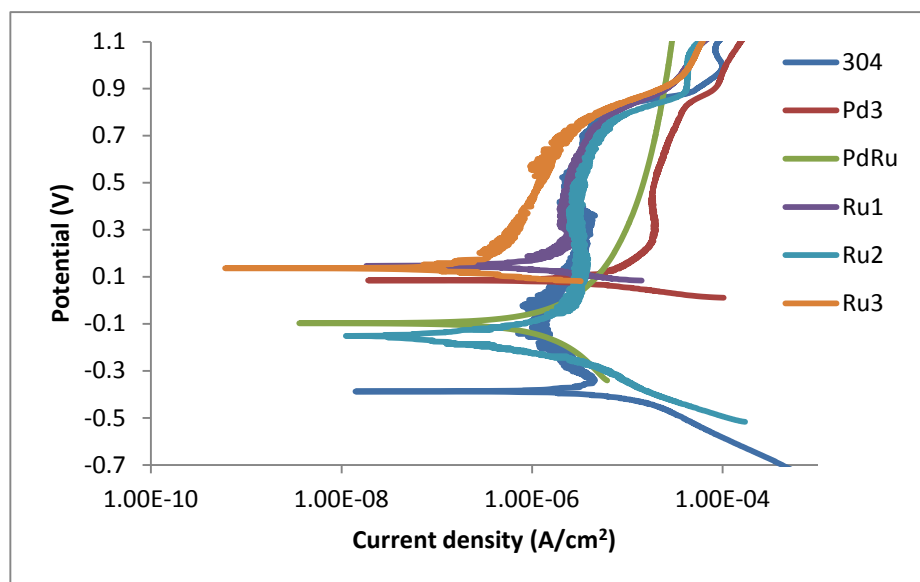
Figure 3. Potentiodynamic scans of the various alloy samples in lactic acid
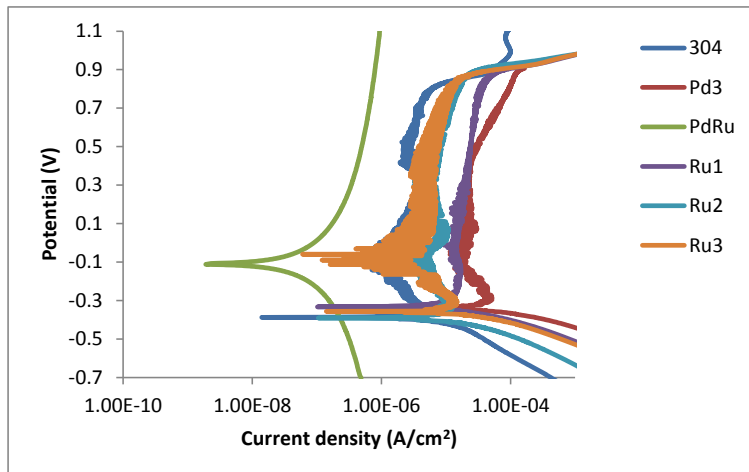
The corrosion behaviour of the sample alloyed with only Pd (Pd3) is similar to that of the base 304 alloy. The alloy sample Ru3 which contained the highest amount of Ru showed the highest corrosion resistance in lactic acid, with the base 304 alloy showing the least resistance. The analysis of the results obtained show that the corrosion resistance of the alloys in lactic acid is increasing in the order of 304 <Pd3<Ru1< PdRu< Ru2<Ru3. It is the only medium in which the alloy with the double PGM addition does not outperform all the alloys with single additions of Ru. Having said this, it should be borne in mind that the corrosion rates are all very similar and of the same order of magnitude.

Table 4. Polarization data obtained for the alloy samples in lactic acid

Corrosion medium	Alloy type	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	βa (V/dec)	$-\beta c$ (V/dec)	Corrosion rate (mm/yr)
Lactic acid	304	-0.3878	0.0190	0.0778	0.6034	0.0400
	Pd3	0.0848	0.0140	0.0310	0.0527	0.0383
	PdRu	-0.0975	0.0036	0.0109	0.0213	0.0044
	Ru1	0.1465	0.0082	0.0453	0.1326	0.0081
	Ru2	-0.1515	0.0011	0.0234	0.0708	0.0024
	Ru3	0.1365	0.0006	0.0430	0.1173	0.0013

3.1.4 Potentiodynamic polarisation of alloys in oxalic acid medium

The potentiodynamic polarization curves for the various 304 alloy samples in 1 M oxalic acid are plotted in Figure 4, while Table 5 shows the E_{corr}, I_{corr}, tafel slopes and corrosion rates derived from the electrochemical tests. It can be observed that a distinctive active-to-passive transition region occurs for nearly all the alloys, except the sample containing both Pd and Ru, in which pseudo passivation is displayed. Higher anodic current densities are observed for all the alloys in oxalic acid compared to the other organic acids investigated. The exception is for the alloy containing the combined Pd and Ru, which showed remarkable corrosion resistance in all the media.

Figure 4. Potentiodynamic scans of the various alloy samples in oxalic acid

The alloy samples containing Pd3 and Ru2 display similar corrosion behaviour in oxalic, citric, acetic and lactic acids. These two alloy samples corroded most in oxalic acid and the least in lactic acid. Similar corrosion behaviour was observed for the base 304 alloy in lactic and oxalic acids. Otero et al. [29] observed and reported similar behavior where the same rates were obtained for powder metallurgy (P/M) steels in lactic and oxalic acids. These could be due to similarity in the molar masses and reactivities of these two acids.

Table 5. Polarization data obtained for the alloy samples in oxalic acid

Corrosion media	Alloy type	E_{corr} (V)	I_{corr} (μA/cm^2)	βa (V/dec)	-βc (V/dec)	Corrosion rate (mm/yr)
Oxalic acid	304	-0.3578	0.1400	0.0709	0.5073	0.1399
	Pd3	-0.3400	0.1280	0.0668	0.4542	0.1316
	PdRu	-0.1133	0.0024	0.0146	0.0330	0.0020
	Ru1	-0.3333	0.1020	0.0653	0.4349	0.1067
	Ru2	-0.3565	0.1050	0.0706	0.5033	0.1460
	Ru3	-0.3910	0.1400	0.0785	0.6141	0.1683

Sample 304 corroded more in acetic and oxalic acids, while sample Pd3 corroded more in citric and oxalic acids compared to their corrosion resistance in lactic acid.

3.2. Potentiometry tests of alloys in acetic acid medium
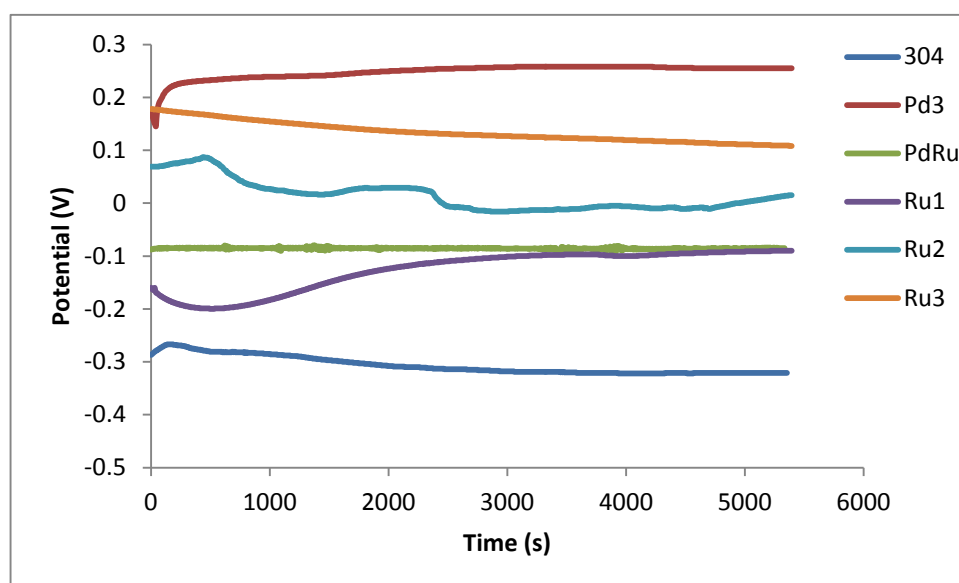
Figure 5. Open circuit potentials with time at zero current in citric acid solution

Open circuit potential measurements versus time were conducted in the different acid media with all the alloys to determine their affinity to corrode over time. Typical responses of the alloys in citric acid are shown in Figure 5 to illustrate the general behaviour observed in all the various acid solutions used in the investigation. It is clear that the open circuit equilibrium established over time does not necessarily correspond to that recorded during the potentiodynamic scans. However, all the alloys display stable behaviour, indicating that the passive film formed on their surfaces remained intact. Often time, stainless steel's resistance in corrosive media is determined by its passive nature and the media to which it is exposed and the inert nature of this passivity (types of oxide films formed on the surface of stainless steels) depends on its stability in the medium of exposure [38-39]. In two cases an increase in open circuit potentials occur over time, which indicated that the alloys

(Ru1 and Pd3) displayed tendencies of spontaneous passivation, a phenomenon well known for cathodically modified alloys in reducing acid media [15].

A comparison of the results obtained in this investigation with others available in the literature employing organic acid media, yields the following:

Table 6. Comparison of typical corrosion rates of 304 and 316 austenitic stainless steels, as well as some duplex stainless steels, in selected organic acid media.

Alloy	Acid Medium	[Acid]	Temp (^{o}C)	Corrosion rate (mm/yr)	Reference
304	1 M Acetic acid	Organic	20±3	0.0901	This work
	1 M Citric acid	Organic	20±3	0.0467	This work
	1 M Lactic Acid	Organic	20±3	0.0400	This work
	1 M Oxalic acid	Organic	20±3	0.1399	This work
Ru3	1 M Acetic acid	Organic	20±3	0.0022	This work
	1 M Citric acid	Organic	20±3	0.1698	This work
	1 M Lactic Acid	Organic	20±3	0.0013	This work
	1 M Oxalic acid	Organic	20±3	0.1683	This work
Pd3	1 M Acetic acid	Organic	20±3	0.1001	This work
	1 M Citric acid	Organic	20±3	0.1389	This work
	1 M Lactic Acid	Organic	20±3	0.0383	This work
	1 M Oxalic acid	Organic	20±3	0.1316	This work
PdRu	1 M Acetic acid	Organic	20±3	0.0007	This work
	1 M Citric acid	Organic	20±3	0.0001	This work
	1 M Lactic Acid	Organic	20±3	0.0044	This work
	1 M Oxalic acid	Organic	20±3	0.0020	This work
304	1 M Oxalic acid	Organic	RTP	0.0815	[28]
316	1 M Oxalic acid	Organic	RTP	0.0446	[28]
2205	80% Acetic acid/0.1%H_2SO_4 with O_2	Organic	20±1	0.0100	[27]
2205	80% Acetic acid/1%H_2SO_4 with O_2	Organic	20±1	0.9000	[27]
2205	1 M Acetic	Organic	RTP	0.0037	[40]
2507	1 M Acetic	Organic	RTP	0.0021	[40]
2205	1 M Formic	Organic	RTP	0.0035	[40]
2507	1 M Formic	Organic	RTP	0.0039	[40]
2205	1 M Citric	Organic	RTP	0.0084	[40]
2507	1 M Citric	Organic	RTP	0.0190	[40]
2205	1 M Oxalic	Organic	RTP	0.0066	[40]
2507	1 M Oxalic	Organic	RTP	0.0170	[40]
2101	1 M H_2SO_4	Inorganic	25	0.0980	[33]
2101LDX/0.15%Ru	1 M H_2SO_4	Inorganic	25	0.0000319	[33]

The alloy which contains both Pd and Ru (PdRu) displayed higher corrosion resistance compared to other alloys in oxalic acid. Alloys Pd3, Ru3 and 304 in the present study showed higher corrosion rates than the duplex stainless steels (2205 and 2507) in the oxalic acid solution. Addition of Pd and Ru (PdRu) improved the corrosion resistance of the studied alloy in all the four organic acids used. The Ru3 alloy generally exhibited better corrosion resistance than the Pd3 alloy in most media. This is in agreement with earlier results in mineral acids in which it was shown that Ru is more effective than Pd to improve the corrosion resistance of stainless steel alloys [16,19]. The 2205 and 2507 duplex stainless steels perform better than the Pd3 alloy and very similar to the Ru3 alloy in acetic acid, but are more corrosion resistant than both Ru3 and Pd3 in citric acid. The duplex stainless steels are much cheaper than either Ru3 and Pd3 and therefore a more economical option in acetic and citric acid media. The duplex alloys, not surprisingly, also outperformed the base 304 in both these acids (citric and acetic). It was only the RuPd alloy that performed better in citric and oxalic acids than the two duplex stainless steels (2205 and 2507) in the work reported to date.

4. CONCLUSIONS

The following conclusions can be drawn from the study on the effect of Pd and Ru addition on the electrochemical behaviour of stainless steels in organic acids at room temperature.

- Pd3 alloy had similar corrosion resistance to Ru1 and Ru2 in all the media tested.
- The PdRu alloy containing both Pd and Ru (0.13% Pd and 0.14% Ru) performed the worse in the lactic acid when considering all the media that it has been tested in.
- The addition of either Pd or Ru generally improved the corrosion resistance of the base 304 stainless steel sample. The corrosion rates of the alloys with PGM additions, especially the PdRu alloy containing both, were generally at least an order of magnitude lower than that of the parent 304 steel in most cases, except in oxalic acid where all the alloys had similar corrosion rates.
- The 304 stainless steel samples corroded the most in oxalic acid, and had similar corrosion rates in citric and lactic acids.
- The duplex stainless steels alloys reported on in an earlier investigation, often perform similar or better than the Ru3 and Pd3 alloys in citric and acetic acid media.
- It is not possible to clearly identify the most aggressive and corrosive organic acid media based on the results obtained in this investigation and those reported in literature, although oxalic acid often resulted in some of the highest corrosion rates measured.
- Although an increase in corrosion resistance in these organic acid media has been obtained by alloying the 304 alloy with Ru and Pd, the increase in corrosion resistance is not nearly as dramatic as has been seen when the media were inorganic mineral acids such as hydrochloric and sulphuric acids.

References

1. G. Back and P. M. Singh, *Corros. Sci.* 46 (2004) 2159.
2. S. Nagarajan and N. Rajendran, *Corros. Sci.* 51 (2009) 217.
3. M. Behpour, S.M. Ghoreishi, N. Soltani and M. Salavati-Niasari, *Corros. Sci.,* 51 (2009) 1073.
4. L.W. Tsay, S.C. Yu, S. D. Chyou and D.Y. Lin, *Corros. Sci.,* 49 (2007) 4028.
5. M. Matula, C. Dagbert, L. Hyspecka, J. Galland and I. Martinakova, *Proceed. Int. Conf. Eurocorros.,* London, (2000) Sept.10–14.
6. I. Betova, M. Bojinov, P. Kinnunen, P. Pohjanne and T. Saario, *Electrochim. Acta* 47 (2002) 3335.
7. A. Galal, N. F. Atta and M. H. S. Al–Hassan, *Mater. Chem. & Phys.* 89 (2005) 38.
8. S. Girija, U. Kamachi Mudali, H.S. Khatak and B. Raj, *Corros. Sci.* 49 (2007) 4051.
9. S. Frangini and S. Loreti, *Corros. Sci.* 49 (2007) 3969.
10. J. J. Dibner and P. Butin, *J. Appl. Poultry Res.* 11 (2002) 453.
11. Y.M. Gunaltun and D. Larrey, Corrosion/2000, NACE, Paper No. 71, NACE International, Houston, TX, 2000.
12. S.D. Zhu, A.Q. Fu, J. Miao, Z.F. Yin, G.S. Zhou and J.F. Wei, *Corros. Sci.* 53 (2011) 3156.
13. L. Xu, Y. Zuo, J. Tang, Y. Tang and P. Ju, *Corros. Sci.* 53 (2011) 3788.
14. R. Z. Zand, K. Verbeken and A. Adriaens, *Prog. Organic Coatings* 72 (2011) 709.
15. J.H. Potgieter, A.M. Heyns and W. Skinner, *J. Appl. Electrochem.* 20 (1990) 711.
16. J.H. Potgieter, *J. Appl. Electrochem.* 21 (1991) 471.
17. P. Baradlai, J.H. Potgieter, W.O. Barnard, L. Tomcsanyi and K. Varga, *Mater. Sci. Forum* 185-188 (1995) 759.
18. E. M. Sherif, J.H. Potgieter, J.D. Comins, L. Cornish, P. A. Olubambi and C.N. Machio, *Corros. Sci.* 51 (2009) 1364.
19. J. H. Potgieter, (Eds. J.A. Richardson, R.A. Cottis, J.D. Scantlebury, S.B. Lyon, P. Skeldon, G.E. Thompson, R. Lindsay and M. Graham.), *Shreir's Corros.* 3 (2010) 2224.
20. J.H. Potgieter, W.O. Barnard, G. Myburg, K. Varga, P. Baradlai and L. Tomcsânyi, *J. Appl. Electrochem.* 26 (1996) 1103.
21. K. Varga, P. Baradlai, W.O. Barnard, G. Myburg, P. Halmos and J.H. Potgieter, *Electrochim. Acta* 42 (1997) 25.
22. G. Myburg, K. Varga, W.O. Barnard, P. Baradlai, L. Tomcsânyi, J.H. Potgieter, C.W. Louw, and M.J. van Staden, *Appl. Surf. Sci.* 136 (1998) 29.
23. P.A. Olubambi, J.H. Potgieter and LA. Cornish, *Mater. & Design* 30 (2009) 1451.
24. S. Chechirlian, P. Eichner and H. Mazille, *Proceed. 11th Inter. Corros. Congress,* 2 (1990) *577.*
25. I. Sekine, S. Hatekeyama and Y. Nakazawa, *Corros. Sci.* 27 (1987) 275.
26. I. Sekine, T. Kawase, M. Kobayashi and M. Yuasa, *Corros. Sci.* 32 (1991) 815.
27. I.J. Invernizzi, E. Sivieri and S.P. Trasatti, *Mater. Sci. & Eng.* 485 (2008) 234.
28. A. S. Afolabi, J. H. Potgieter, A. S. Abdulkareem and N. Fungura, *Proceed Inter. Conf. Indust. Eng. & Systems Manag. Paris, France July 27-29, 2011,* 79 (2011) 87.
29. E. Otero, A. Pardo, M. V. Utrilla, F. J. Perez and C. Merino, *Corros. Sci.* 39 (1997) 453.
30. J.H. Potgieter, N. Thanjekwayo, P. Olubambi, N. Maledi and S.S. Potgieter-Vermaak, *J. Hard Metals & Refrac. Mater.* 29 (2011) 478.
31. F. Scenini, K. Govender, S. Lyon and A. Sherry, *Corros. Eng., Sci. & Technol.* 47 (2012) 498.
32. K. Govender, F. Scenini, S. Lyon and A. Sherry, *Corros. Eng., Sci. & Technol.* 47 (2012) 507.
33. O.A. Olaseinde, J.W. Van der Merwe, L.A. Cornish, L.H. Chown, and P.A. Olubambi, *J. South Afri. Inst. Min. Metall.* 7A (2012) 535.
34. Y. Garsany, D. Pletcher and B. Hedges, Corrosion/2002, NACE, Paper No. 02273, NACE International, Houston, TX, 2002.

35. M. Matos, C. Canhoto, M. Bento and M. Geraldo, *J. Electroanal. Chem.* 647 (2010) 144.
36. S.A.Abd El–Maksoud, *Int. J. Electrochem. Sci.* 3 (2008) 528.
37. T. Tran, B. Brown, S. Nesic, B. Tribollet, Corrosion/2013, NACE, Paper No.2487, NACE International, Houston, TX, 2013.
38. M. Matula, L. Hyspecka, M. Svoboda, V. Vodarek, C. Dagbert, J. Galland, Z. Stonawska, and L. Tuma, *Mater. Charact.* 46 (2001) 203.
39. G.H. Aydogdu, and M.K. Aydinol, *Corros. Sci.* 48 (2006) 3565.
40. F.V. Adams, P.A. Olubambi, J.H. Potgieter and J. Van Der Merwe, *Anti-Corros. Methods Mater.* 57 (2010) 107.