

## Corrosion Behavior of Duplex Stainless Steel Alloy Cathodically Modified with Minor Ruthenium Additions in Concentrated Sulfuric Acid Solutions

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The corrosion behavior of duplex stainless steel (DSS, Fe - 22%Cr - 9%Ni - 3%Mo) alloy after varying exposure periods in 10% H<sub>2</sub>SO<sub>4</sub> solution was investigated. The influences of minor Ru additions, namely, 0.14%, 0.22%, and 0.28%, on the passivation of this DSS were also reported. The study was performed using open-circuit potential, potentiodynamic polarization, potentiostatic current-time, electrochemical impedance spectroscopy, and weight loss measurements. Electrochemical measurements indicated that the presence of Ru passivated the DSS alloy by decreasing its corrosion parameters. This effect remarkably increased with increasing the Ru content as well as the immersion time of DSS in the chloride solution before measurements. Weight-loss time data after varied exposure intervals (24 – 168 h) confirmed the electrochemical ones and showed that the weight-loss and corrosion rate of DSS significantly decreased in the presence of Ru and the increase of its content in the DSS alloy.

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**Keywords:** Corrosion, duplex stainless steel, electrochemical measurements, ruthenium additions, sulfuric acid solutions, weight-loss tests

### 1. INTRODUCTION

Duplex stainless steels (DSSs) are called “duplex” because they have a two-phase microstructure, which consists of grains of ferritic and austenitic stainless steel. DSSs are characterized by their high strength, which is about twice the regular austenitic or ferritic stainless steels, and non-hardenable by heat treatment. In addition DSSs have excellent corrosion resistance, especially in

oxidizing media and conditions conducive to localized corrosion [1-5]. The fact that they possess an outstanding combination of mechanical strength, corrosion resistance in various types of environments and weldability makes DSSs suitable for many industrial applications like chemical plants, nuclear reactors, offshore platforms, oil and gas production and process systems [6, 7]. The high strength of DSSs enables both weight and cost savings when they are used as corrosion resistant materials in constructions [5-9].

It has been reported [1-3, 9-12] that the corrosion resistance of virtually all stainless steels can be remarkably increased by alloying them with minor additions of platinum group metals (PGMs). Sufficient amounts of these alloying elements are able to retard the anodic dissolution of steels to which they are added and also increase the effectiveness of cathodic processes owing to the reduced overvoltage of hydrogen on them.

The present work reports the effects of minor Ru additions on the passivation of DSS corrosion in 10% H<sub>2</sub>SO<sub>4</sub> solutions. The fact that ruthenium is the cheapest of the PGMs perpetuates the interest in the spontaneous passivation processes of steels containing small amounts of Ru as alloying element [11-16]. In the current study, the addition of Ru to DSS was expected to improve the corrosion resistance of the alloy as a result of the ability of Ru to inhibit the anodic reactions as well as modify the efficiency of the cathodic process of the alloy. The investigation has been carried out using open-circuit potential, potentiodynamic polarization, potentiostatic current-time, EIS, and weight-loss measurements.

## 2. EXPERIMENTAL PROCEDURE

A stock solution of 10% of sulfuric acid was prepared from an as received 96% H<sub>2</sub>SO<sub>4</sub>. The duplex stainless steel alloys (DSSs) used in this investigation were having the composition, Fe-22%Cr-9%Ni-3%Mo containing 0.00% (alloy 1), 0.14% (alloy 2), 0.22% (alloy 3), and 0.28% Ru (alloy 4), respectively.

The DSSs alloys were prepared in a Leybold Heraeus vacuum furnace from electrolytic iron, chromium, ferromolybdenum and nickel, as well as sponge ruthenium, under an argon atmosphere. After degassing of the raw material in a magnesia crucible, the temperature of the charge was increased to between 1610 - 1670 °C, and the molten material was cast into a steel mold. After cooling, samples were taken to check the bulk homogeneity. Once bulk homogeneity was confirmed, the alloys were hot-rolled from an original thickness of about 45 mm to between 3-5 mm. Rolling took place in a series of stages of a maximum of 3 passes at a time before reheating the ingot, until the desired thickness was obtained.

A three-electrode electrochemical cell was employed. The DSS alloy, a platinum foil, and an Ag/AgCl electrode (in 3M KCl) were used as working, counter, and reference electrodes, respectively. The DSS samples for electrochemical measurements were prepared by attaching an insulated copper wire to one face of the sample using an aluminium conducting tape, and cold mounted in resin. The samples were then left to dry in air for 24 h at room temperature.

Before measurements, the DSS electrodes were polished successively with metallographic emery paper of increasing fineness of up to 1000 grits. The electrodes were then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again and finally dried with a stream of dry air. In order to prevent the possibility of crevice corrosion during measurement, the interface between sample and resin was coated with Bostik Quickset, a polyacrylate resin. Working DSS electrodes had rectangular dimensions of 1 x 1 x 0.4 cm, with total exposed area of 1 cm<sup>2</sup>.

Electrochemical experiments were performed by using an Autolab Potentiostat (PGSTAT20 computer controlled) operated by the general purpose electrochemical software (GPES) version 4.9. The potentiodynamic polarization curves were collected by scanning the potential in the forward direction from -600 to +1200 mV against Ag/AgCl at a scan rate of 3.0 mV/s; the potential was then reversed in the backward direction at the same scan rate. Potentiostatic current-time measurements at constant anodic potential were carried out by stepping the potential of DSSs alloys to +1000 mV versus Ag/AgCl. Electrochemical impedance spectroscopy data were obtained at an open circuit potential value over a frequency range from 100000 Hz to 0.1Hz, with an ac wave of  $\pm 5$  mV peak-to-peak overlaid on a dc bias potential, and the impedance spectra were collected using Powersine software at a rate of 10 points per decade change in frequency.

All electrochemical experiments were performed at room temperature in naturally aerated solutions and the data were obtained after 1 h and 72 h immersions in the test electrolytes before measurements. Only, open-circuit potential (OCP) measurements were recorded from the first moment of immersion and for 24 h continuously.

The weight loss experiments were carried out using cylindrical DSSs coupons having dimensions of 1.5 cm diameter and 0.3 cm height with an exposed total area of 4.95 cm<sup>2</sup>. The coupons were drilled then polished and dried as DSS rods for electrochemical tests were. The coupons then weighed ( $m_1$ ), after which it was suspended in 100 cm<sup>3</sup> solutions of 10% H<sub>2</sub>SO<sub>4</sub> using thin glass hooks for varied exposure periods (24 – 168 h). At the end of a run, the samples were rinsed with distilled water, cleaned with acetone to remove the corrosion products formed on the surface, dried and weighed again ( $m_2$ ). All weight-loss measurements were performed in triplicate and the maximum standard deviation in the observed weight loss was  $\pm 1.5\%$ . The values of the loss in weight per area ( $\Delta m$ ) and the corrosion rate ( $K_{\text{Corr}}$ ) for DSS coupons in 10% sulfuric acid solutions were calculated as follows [1, 2, 17-19]:

$$\Delta m = \frac{m_1 - m_2}{A} \quad (1)$$

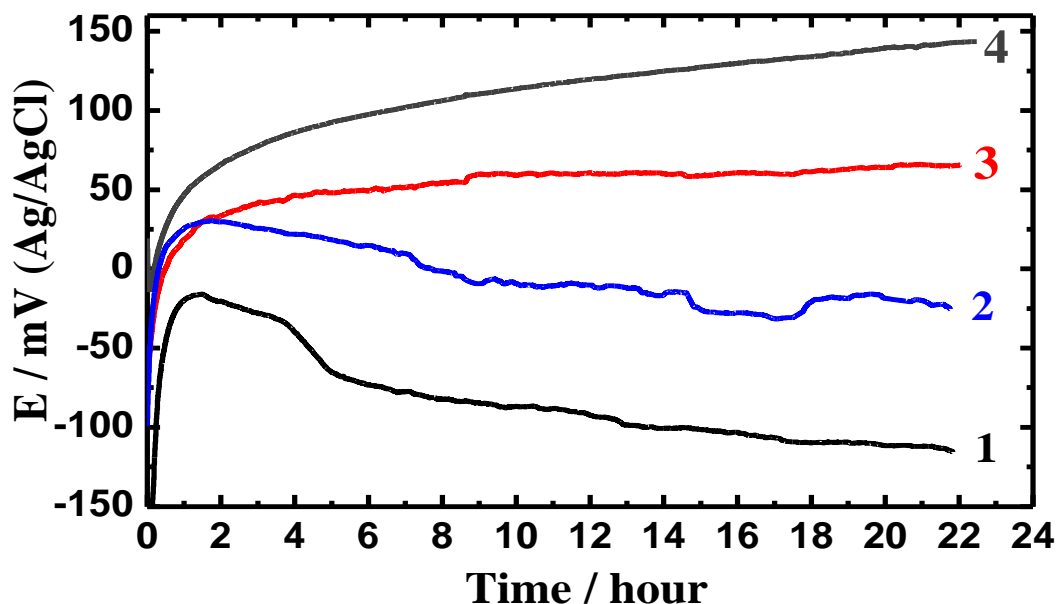
$$K_{\text{Corr}} = K \left( \frac{m_1 - m_2}{DA t} \right) \quad (2)$$

Where,  $m_1$  and  $m_2$  are the weights of the DSS coupon per gram before and after its immersion in the test solution, respectively;  $A$  is the area of the DSS coupon per cm<sup>2</sup>;  $K$  is the constant that defines the unit of the corrosion rate ( $K = 8.76 \times 10^4$  for the mmpy unit);  $D$  is the density of DSS per g/cm<sup>3</sup>; and  $t$  is the immersion time per hour.

### 3. RESULTS AND DISCUSSION

#### 3.1. Open-circuit potential (OCP) measurements

Fig. 1 shows the variation of the OCP of the DSS alloy 1 (1), alloy 2 (2), alloy 3 (3) and alloy 4 (4) in 10%  $\text{H}_2\text{SO}_4$  solutions versus time. The OCP of DSS alloy 1, curve 1, shifted towards the less negative values in the first 30 min.



**Figure 1.** Variation of the open-circuit potential versus time for the duplex stainless steel, (1) alloy 1, (2) alloy 2, (3) alloy 3, and (4) alloy 4, respectively in 10%  $\text{H}_2\text{SO}_4$  solutions.

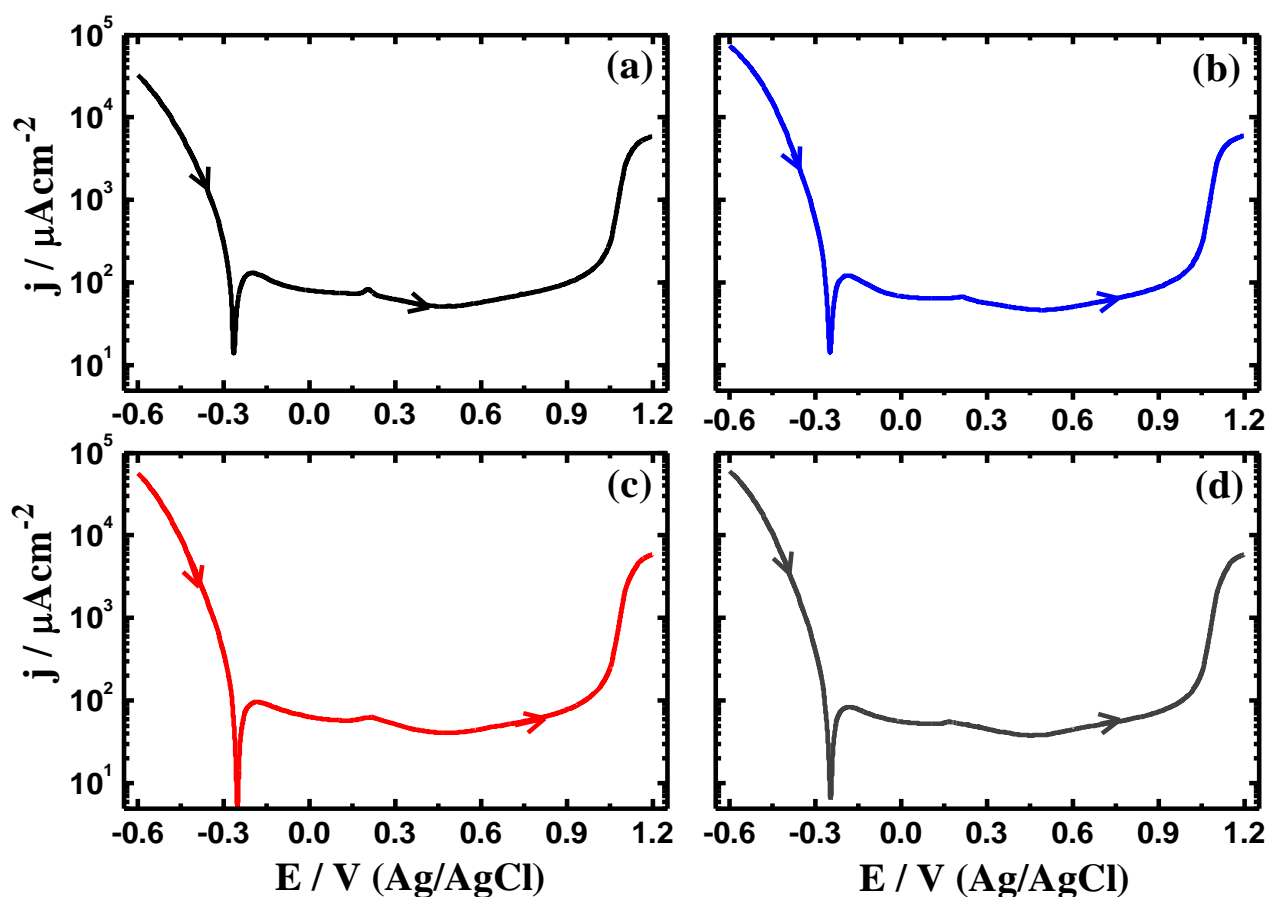
This shift may have resulted from the resistance of the alloy due to presence of an oxide film was formed on its surface in air before the alloy immersion. The potential then started to negatively move to the more active values for the whole time of the experiment, which is probably due to the severe dissolution of the alloy surface by the aggressiveness action of  $\text{H}_2\text{SO}_4$ . This DSS behavior indicates that alloy 1 suffers uniform corrosion and does not give any indication of the occurrence of pitting type corrosion.

In the presence of 0.14% Ru, alloy 2 (curve 2) the OCP showed almost similar behavior except that the potential values were recorded at more positive values compared to alloy 1 at all times. This means that the presence of Ru at that concentration increased the corrosion resistance of the alloy. Further increase the Ru content, 0.22%, alloy 3 as seen in curve 3, shifted the potential towards the more positive values up on the alloy immersion with continued positive shifts with increasing time and this effect was increased by increasing Ru to 0.28% as can be seen on curve 4, alloy 4. This indicates that the presence of Ru and the increase of its content remarkably decrease the uniform corrosion of DSS alloy. This agrees with the previous work [1-3, 12-14], which stated that, stainless steels with Ru as minor alloying component are passivated spontaneously due to the formation of passive layers of

remarkably increased corrosion resistance on their surfaces, which shift the corrosion potential of these alloys toward the more positive values.

### 3.2. Potentiodynamic polarization measurements

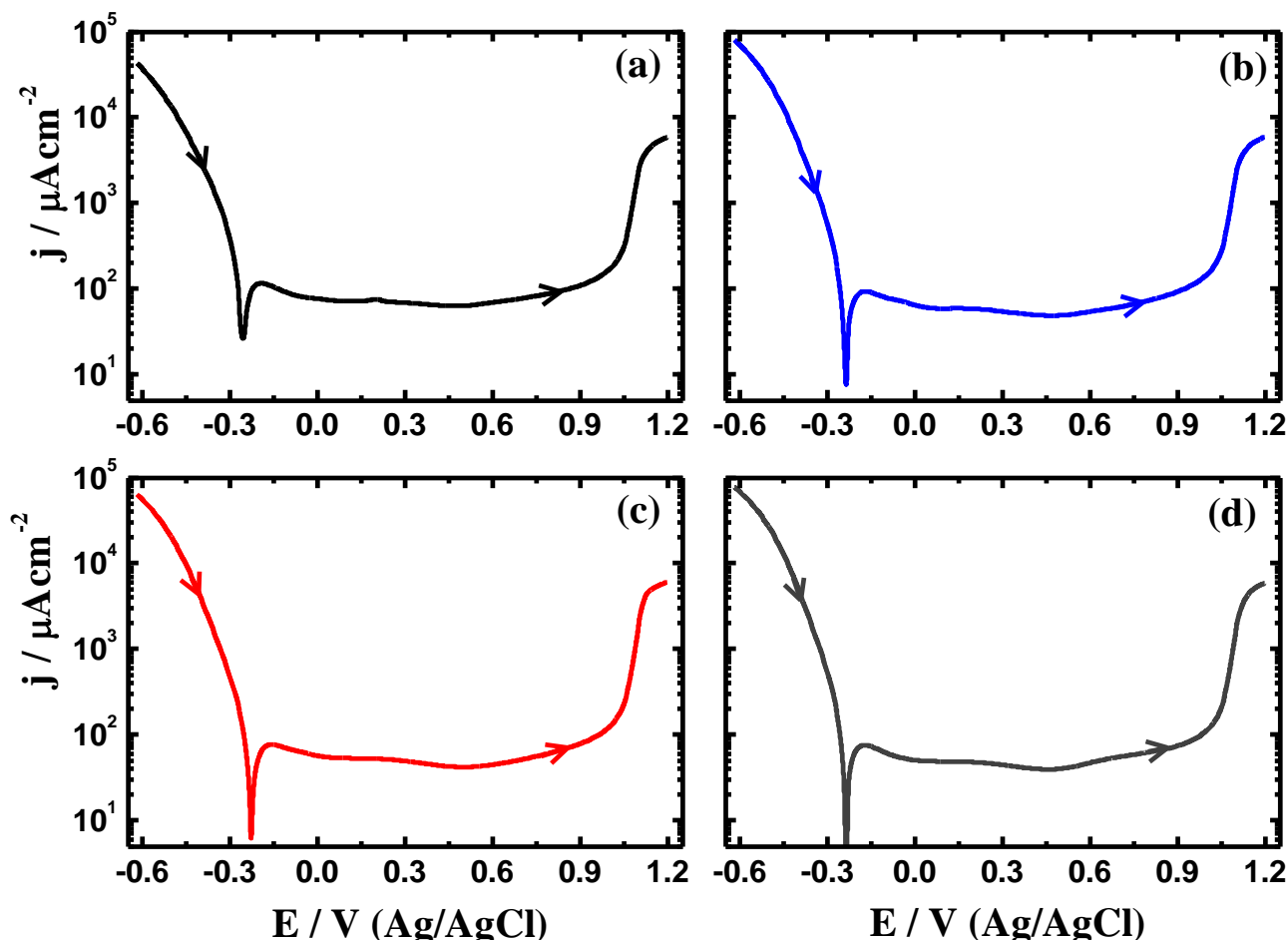
The polarization curves for alloy 1 (a), alloy 2 (b), alloy 3 (c) and alloy 4 (d) when the measurements were recorded after 20 min of the electrode immersion in 10% H<sub>2</sub>SO<sub>4</sub> are shown in Fig. 2.



**Figure 2.** Potentiodynamic polarization curves for the duplex stainless steel, (a) alloy 1, (b) alloy 2, (c) alloy 3, and (d) alloy 4, respectively after their immersions in 10% H<sub>2</sub>SO<sub>4</sub> solutions for 20 min.

The polarization curves obtained at the same conditions after 72 h of the alloy immersion are also depicted in Fig. 3. These experiments were carried out to understand the effect of the minor Ru additions as well as the length of the immersion time on the corrosion parameters of the DSS alloy in the sulfuric acid test solutions. The values of corrosion potential ( $E_{Corr}$ ), cathodic Tafel slope ( $\beta_c$ ), anodic Tafel slope ( $\beta_a$ ), corrosion current density ( $j_{Corr}$ ), critical potential ( $E_{Crit}$ ), critical current ( $j_{Crit}$ ), passivation current density ( $j_{Pass}$ ), polarization resistance ( $R_p$ ), and corrosion rate ( $K_{Corr}$ ), in addition to

percentages of protection efficiency ( $PE\%$ ), were calculated from polarization curves shown in Fig. 2 and Fig. 3 and listed in Table 1.



**Figure 3.** Potentiodynamic polarization curves for the duplex stainless steel, (a) alloy 1, (b) alloy 2, (c) alloy 3, and (d) alloy 4, respectively after their immersions in 10%  $H_2SO_4$  solutions for 72 h.

The values of  $j_{Corr}$  and  $E_{Corr}$  were obtained from the extrapolation of anodic and cathodic Tafel lines located next to the linearized current regions. The values of  $R_p$  and  $K_{Corr}$  were calculated as reported in our previous studies [17-23]; in this case, the value of the equivalent weight of the DSS alloy (calculated  $E_w = 24.6$  grams/equivalent), the area of DSS exposed to the test solution ( $A = 1$   $cm^2$ ), and the density of the DSS alloy ( $D = 8.03$   $g/cm^3$ ) had to be known. The values of  $PE\%$  were also obtained as in reported in the earlier work as follows [1, 2],

$$PE\% = \frac{j_{Corr}^1 - j_{Corr}^2}{j_{Corr}^1} \times 100 \quad (3)$$

Here  $j_{Corr}^1$  and  $j_{Corr}^2$  are the corrosion currents for the DSS alloys in the absence and presence of Ru, respectively.

**Table 1.** Corrosion parameters obtained from polarization curves shown in Fig. 2 and Fig. 3 for the DSS alloys after 20 min and 72 h of the electrode immersion in 10% H<sub>2</sub>SO<sub>4</sub> solutions.

Alloy	Parameter									
	E <sub>Corr</sub> / mV	j <sub>Corr</sub> / μA cm <sup>-2</sup>	β <sub>c</sub> / mV dec <sup>-1</sup>	β <sub>a</sub> / mV dec <sup>-1</sup>	E <sub>Crit</sub> / mV	j <sub>Crit</sub> / μA cm <sup>-2</sup>	j <sub>Pass</sub> / μA cm <sup>-2</sup>	R <sub>p</sub> / Ω cm <sup>2</sup>	K <sub>Corr</sub> / mmy <sup>-1</sup>	PE / %
1 (20 min)	-248	95	85	98	-200	135	72.7	0.208	0.952	—
2 (20 min)	-232	85	87	100	-190	120	64.5	0.238	0.852	10.53
3 (20 min)	-228	70	90	105	-182	95	57.1	0.301	0.702	26.32
4 (20 min)	-225	55	95	115	-180	83	51.4	0.411	0.551	42.11
1 (72 h)	-238	75	90	130	-198	120	72.4	0.308	0.752	—
2 (72 h)	-228	67	95	135	-170	92	60.8	0.362	0.672	10.67
3 (72 h)	-222	54	100	140	-160	77	52.2	0.470	0.541	28.00
4 (72 h)	-220	43	100	146	-167	75	49.6	0.600	0.431	42.67

The DSS alloy 1 (Fig. 2, curve 1) shows a large passive region in the anodic branch as a result of the high corrosion resistance of the alloy to the aggressiveness attack of the acid to the surface. At a certain potential value the current rapidly increases due to the active dissolution of the alloy under the influence of the high anodic potential and the corrosivity of the sulfuric acid. It is generally believed that the cathodic reaction for metals and alloys in sulfuric acid solutions is the hydrogen evolution according to the following equation [2],



The electrons consumed at the cathode due to the hydrogen ion reduction are produced during the dissolution of the alloy in the corrosive acid medium through the anodic reaction as follows,

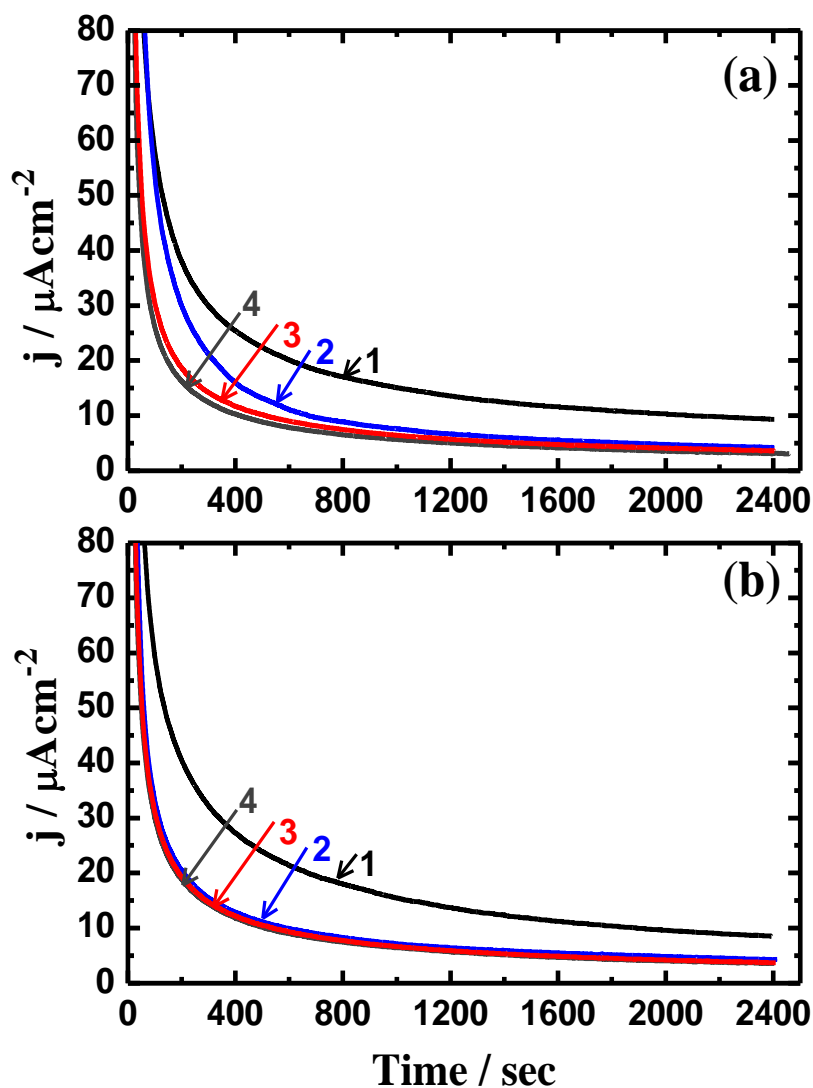


These reactions are reduced by the presence of Ru and the increase of its content. This is clearly seen from Fig. 2 and Table 1, where the values of E<sub>Corr</sub> shifted to the less negative and the values of j<sub>Corr</sub>, j<sub>Prot</sub>, j<sub>Pass</sub>, and K<sub>Corr</sub> decreased. On the other hand, the values of R<sub>p</sub> increased in the presence of Ru and upon the increase of its percentage in the alloy. The values of PE% increased from circa 10% to about 42% with increasing the Ru from 0.14% to 0.28%.

Increasing the immersion time before measurements to 72 h, Fig. 3, led to decreasing the corrosion of DSS (curve 1) compared to the short time (Fig. 2 curve 1) as a result of decreasing the uniform attack, which is might be due to the formation of corrosion products on the surface of the alloy. It is also seen from Fig. 3 and Table 1 that the presence of Ru with increased contents provided further protection for the alloy surface as the values of j<sub>Corr</sub> and K<sub>Corr</sub> recorded lower values. This effect also shifted E<sub>Corr</sub> to the less negative values and increased the values of R<sub>p</sub> as well as decreased j<sub>Prot</sub> and j<sub>Pass</sub>.

In general, the decreases we have seen in the cathodic,  $j_{Corr}$ , anodic,  $j_{Prot}$ , and  $j_{Pass}$  currents and  $K_{Corr}$  with increasing Ru content and further with immersion time are mainly due to the passivation of the DSS by Ru [1, 2]. The positive shift in the  $E_{Corr}$  is apparently due to increasing the effectiveness of cathodic processes, which in turn decrease the rate of the anodic reactions [1-3]. This can be explained according to the previous studies [1, 2, 16, 24], which stated that the presence of Ru in the steel leads to a possible interaction of Ru with Fe permitting the free diffusion of Cr to the surface. This passivates the surface and increases its resistance against corrosion in the solution under investigation. Another explanation has been reported by Tjong et al. [25] that the presence of Ru in the steel allows Ru to be taken up in the scale, resulting in a thin, compact film, which could decrease the uniform corrosion of the DSS alloy in the sulfuric acid solution.

### 3.3. Potentiostatic current-time measurements



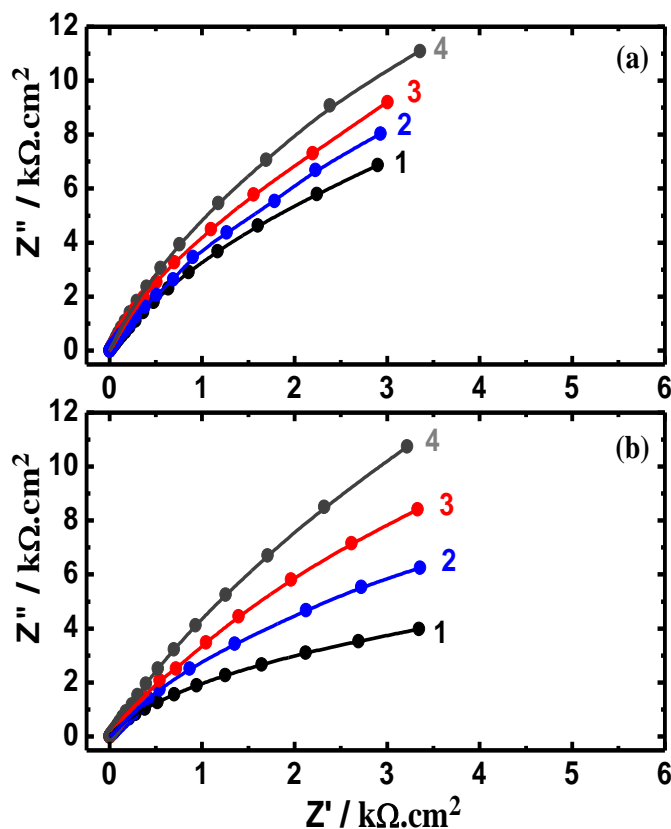
**Figure 4.** Potentiostatic current-time curves obtained at 1.0 V vs. Ag/AgCl for the duplex stainless steel, (1) alloy 1, (2) alloy, (3) alloy and (4) alloy 4 after their immersions in 10%  $H_2SO_4$  solutions for (a) 20 min and (b) 72 h, respectively.



In order to shed more light on the dissolution of DSS in 10% H<sub>2</sub>SO<sub>4</sub> and the effect of Ru additions on the alloy passivation at a more positive potential value, potentiostatic current-time experiments were carried out at 1000 mV vs. Ag/AgCl. The variation of the dissolution currents of alloy 1 (1), alloy 2 (2), alloy 3 (3), and alloy 4 (4) with time at 1000 mV after 20 min (a) and 72 h (b) immersion in 10% H<sub>2</sub>SO<sub>4</sub> solutions are shown in Fig. 4.

It is seen from Fig. 4 that the highest current values were recorded for DSS alloy 1 (curve 1) both after 20 min and 72 h immersion in the test electrolyte. Where, the initial current that was obtained upon the potential application started at high values and rapidly decreased in the first four hundred seconds. The current then slowly decreased with increasing the experimental time. In the presence of 0.14% Ru (curve 2), the absolute current values decreased across the whole time of the run. Further Ru increments (curves 3 and 4) provided further decreases in the absolute currents. Increasing the immersion time of the DSS alloys to 72 h before measurement (Fig. 4b), showed nearly similar behaviour but with lower absolute current values, especially with those having Ru. This is in a good agreement with the data obtained by potentiodynamic polarization, where the corrosion potential shifted to negative values, while corrosion and passivation currents decreased in the presence of Ru and with increasing its content as well as immersion time to 72h.

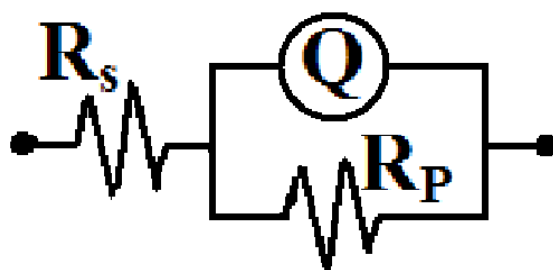
### 3.4. Electrochemical impedance spectroscopy (EIS) measurements



**Figure 5.** Nyquist plots obtained for the duplex stainless steel, (1) alloy 1, (2) alloy, (3) alloy and (4) alloy 4 after their immersions in 10% H<sub>2</sub>SO<sub>4</sub> solutions for (a) 20 min and (b) 72 h, respectively; symbols represent the actual data and solid lines represent the best fit.

The EIS was successfully employed in our previous studies to explain the corrosion and corrosion inhibition of duplex stainless steel [1, 2], copper [26-30], aluminium [31, 32], iron [23] and magnesium [17] in chloride media.

The current EIS experiments were carried out to confirm the data obtained by polarization and potentiostatic current-time measurements. Typical Nyquist plots obtained for (1) DSS alloy 1, (2) alloy 2, (3) alloy 3, and (4) alloy 4 after their immersions in 10% H<sub>2</sub>SO<sub>4</sub> solutions for (a) 20 min and (b) 72 h, respectively are shown in Fig. 5. These spectra were analysed by best fitting to the equivalent circuit model shown in Fig. 6.



**Figure 6.** The equivalent circuit model used to fit the experimental data presented in Fig. 4. The physical meanings for symbols used in the circuit are reported in the text.

The elements of the equivalent circuit can be defined as:  $R_s$  represents the solution resistance,  $R_p$  the polarization resistance and can be defined also as the charge transfer resistance, and  $Q$  the constant phase elements (CPEs). The obtained values of  $R_s$ ,  $R_p$  and  $Q$  from the circuit shown in Fig. 6 for the DSS alloy in absence and presence of Ru after 20 min and 72 h immersion in sulfuric acid are listed in Table 2.

**Table 2.** EIS parameters obtained by fitting the Nyquist plots shown in Fig. 5 with the equivalent circuit model shown in Fig. 6 for the DSS alloys in 10% H<sub>2</sub>SO<sub>4</sub> solutions.

Parameter	Time	20 minutes				72 hours			
Alloy Number		Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 1	Alloy 2	Alloy 3	Alloy 4
$R_s / \Omega \text{ cm}^2$		0.93	1.07	1.14	1.36	0.97	1.1	1.24	1.43
$Q$	$Y_Q / \mu\text{F cm}^{-2}$	18.4	16.2	14.9	13.7	17.3	15.2	12.8	11.6
	$n$	0.86	0.88	0.88	0.91	0.86	0.9	0.9	0.91
$R_p / \Omega \text{ cm}^2$		4420	5667	8243	10309	4921	6284	8963	11162

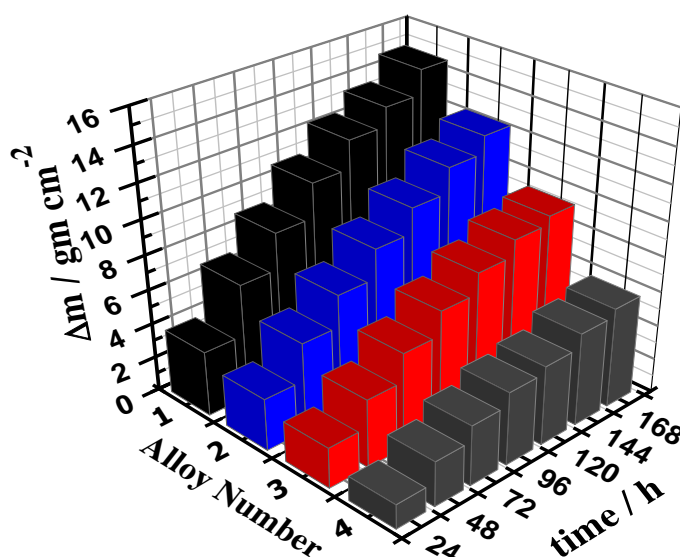
It is seen from Fig. 5 and Table 2 that the  $R_s$  and  $R_p$  values recorded for alloy 1 increased as the immersion time was increased. The constant phase elements (CPEs,  $Q$ ) with their  $n$  values close to one ( $n = 0.86$ ) represent double layer capacitors with some pores. The CPEs decreased a little with

increasing immersion time due to the coverage of the charged surface with the corrosion products formed on the surface with time, which in turn reduces the capacitive effects [33, 34]. The presence of 0.14% Ru, alloy 2, raises the values of  $R_s$  and  $R_p$  with further increases seen with increasing the Ru content as well as the immersion time. The CPEs ( $Q$ ) with their  $n$  values increased from 0.86 to 0.91 represent double layer capacitors with some pores. The gradual decrease of CPEs with Ru and upon increase in its content in the alloy indicates that the surface is more protected due to the lower capacitive effects. This was also confirmed by the semicircles at high frequencies, which are generally associated with the relaxation of electrical double layer capacitors. Moreover, the diameters of the high frequency semicircles can be considered as the charge transfer resistance ( $R_p$ ) [35].

The protection of DSS alloy with time is attributed to the partial protection of the alloy with time due to the formation of corrosion products on its surface. The steady increase in the polarization resistance of the electron transfer reaction upon increasing the Ru content is in general agreement with the positive shift in the corrosion and protection potentials [1, 2]. The decrease of CPEs and the increase of their  $n$  values and also the increase of  $R_s$  and  $R_p$  values with both time and Ru content are in general agreement with polarization (Fig. 2, Fig. 3 and Table 1) and current-time measurements (Fig. 4). Where, this effect led to the decrease in corrosion parameters such as  $j_{\text{Corr}}$ , dissolution currents and  $K_{\text{Corr}}$ , as well as, the increase in polarization resistance,  $R_p$ , values under the same conditions. In fact, the agreement of EIS and polarization data is because the EIS measurements do not disturb the alloy surface as it was carried out at the open-circuit potential of the alloy.

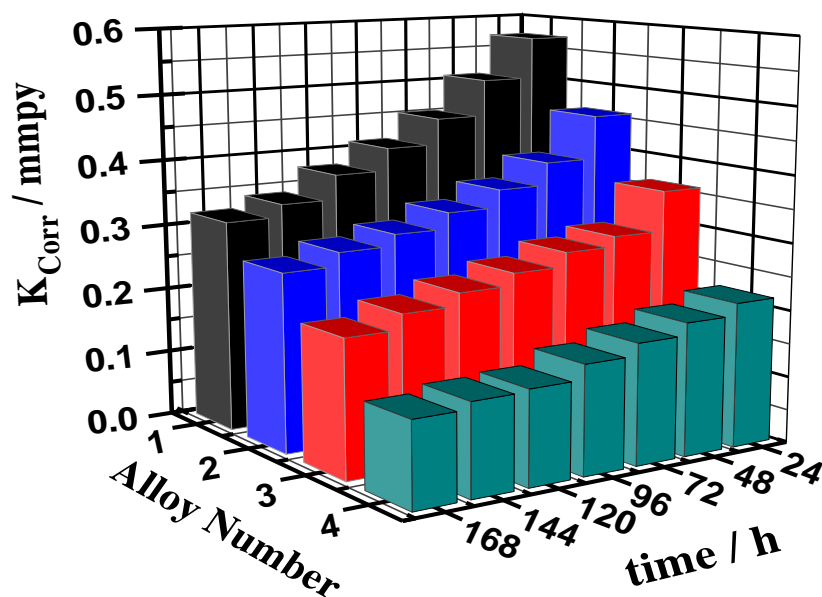
### 3.5. Weight-loss measurements

The variation of the measured weight loss ( $\Delta m$ ,  $\text{mg cm}^{-2}$ ) versus time between 24 h and 168 h for the DSS coupons in 300 ml of 10%  $\text{H}_2\text{SO}_4$  solutions are depicted in Fig. 7.



**Figure 7.** Variation of the loss of weight ( $\Delta m$  /  $\text{gm.cm}^{-2}$ ) as a function of time for the different duplex stainless steel alloys in 10%  $\text{H}_2\text{SO}_4$  solutions.

The change of the calculated corrosion rate ( $K_{Corr}$ , millimeters per year, ( $mm\text{y}^{-1}$ )) as a function of time over the different exposure periods is also shown in Fig. 8.



**Figure 8.** Change of the corrosion rate ( $K_{Corr}$ , millimeters per year, ( $mm\text{y}^{-1}$ )) versus time for the duplex stainless steel alloys in 10%  $\text{H}_2\text{SO}_4$  solutions.

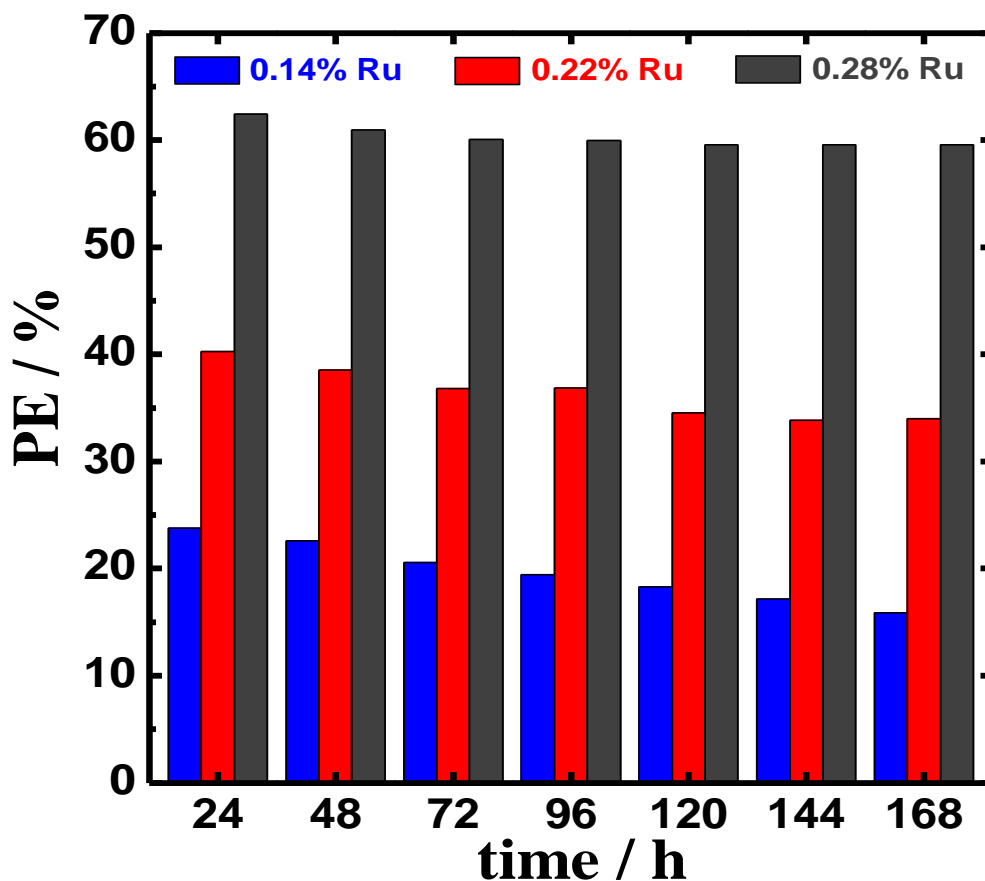
The values of both  $\Delta m$  and  $K_{Corr}$  were obtained using equation 1 and equation 2, respectively. It is seen from Fig. 7 that the values of  $\Delta m$  linearly increased with time for the DSS alloy 1 due to its continuous dissolution in the sulfuric acid solution. The presence of 0.14% Ru (alloy 2) considerably reduced the aggressiveness attack of the sulfuric acid solution, which reflected on decreasing the dissolution of the alloy by lowering the increase in  $\Delta m$  values with time. This effect was highly enhanced in the presence of 0.22% Ru (alloy 3) and further with the increase of Ru content to 0.28% (alloy 4).

Although the weight loss of DSS alloy 1 increased in the sulfuric solution (Fig. 7), its corrosion rate decreased with time (Fig. 8) due to the formation of corrosion products on the surface of the alloy. These corrosion products are not compact enough and only produce partial passivation as indicated by polarization and EIS data. Addition of 0.14% Ru, alloy 2, decreased the values of  $K_{Corr}$  for all exposure periods compared to alloy 1. Further significant decreases in the values of  $K_{Corr}$  were recorded in the presence of Ru and with the increase in its content in the DSS alloy. This provides another indication that the presence of Ru highly passivated the DSS alloy and its efficiency increases with increasing its content in the alloy.

The ability of Ru in increasing the passivation of DSS alloy in 10% sulfuric acid solutions was further confirmed by calculating the passivation efficiency. The values of  $PE\%$  of Ru for the DSS alloy were obtained as in the case of inhibition efficiency using the following equation [1, 2, 32, 36];

$$PE\% = \frac{K_{Corr}^0 - K_{Corr}^R}{K_{Corr}^R} \times 100 \tag{6}$$

Where,  $K_{Corr}^0$  and  $K_{Corr}^R$  are the corrosion rates of the DSS alloy in the absence and presence of Ru, respectively. The variation of PE% as a function of time for the DSS alloy by 0.14%, 0.22%, and 0.28% Ru in 10%  $H_2SO_4$  solution is shown in Fig. 9.



**Figure 9.** Variation of the protection efficiency (PE%) against time for the duplex stainless steel alloy by 0.14%, 0.22%, and 0.28% Ru in 10%  $H_2SO_4$  solutions.

The presence of Ru at lower contents revealed that the alloy can be passivated for reasonable extent. Increasing the Ru content remarkably increases the resistance of the alloy against corrosion by increasing the values of PE%. On the other hand, increasing the exposure time slightly decreases the ability of Ru in protecting the DSS surface. The maximum passivation of DSS by Ru is obtained at early stages of the alloy immersion in the test solution in the presence of 0.28% Ru. This means that the presence of Ru and the increase of its content increase the passivation of the DSS alloy in the corrosive test solution, which is in a good agreement with the measurements obtained by polarization and EIS investigations.

#### 4. CONCLUSIONS

Corrosion and corrosion passivation of duplex stainless steel alloy having 0.00%, 0.14%, 0.22%, and 0.28% of ruthenium after varied exposure intervals in 10% H<sub>2</sub>SO<sub>4</sub> solutions have been studied using conventional electrochemical, electrochemical impedance spectroscopy and gravimetric techniques. Open-circuit potential measurements showed large positive shifts in the corrosion potential of the alloy with the presence of Ru and the increase of its content. Polarization and current-time measurements indicated that increasing the immersion time before measurement decreases the uniform corrosion of the alloy. The presence of Ru and the increase of its content increase the resistance of the alloy against corrosion by reducing the corrosion current density and corrosion rate and increasing the polarization resistance as well as shifting the corrosion and protection potentials to more positive values. Impedance spectra revealed that prolonging the immersion time and the addition of Ru and the increase of its content highly raise the surface and polarization resistances. Weight-loss data proved that the presence of Ru remarkably decreases the loss of weight and corrosion rate of the alloy over 168 h of the coupons immersion. Both electrochemical and weight loss data are collectively in good agreement and show clearly that the corrosion rate of DSS decreases with time and the addition of Ru and the increase of its content greatly protect the alloy against general corrosion in the 10% H<sub>2</sub>SO<sub>4</sub> solutions.

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