



# Surface composition of Ru containing duplex stainless steel after passivation in non-oxidizing media

G. Myburg<sup>a,\*</sup>, K. Varga<sup>b</sup>, W.O. Barnard<sup>a</sup>, P. Baradlai<sup>b</sup>, L. Tomcsányi<sup>c</sup>,  
J.H. Potgieter<sup>d</sup>, C.W. Louw<sup>e</sup>, M.J. van Staden<sup>e</sup>

<sup>a</sup> Department of Physics, University of Pretoria, Pretoria 0002, South Africa

<sup>b</sup> Department of Radiochemistry, University of Veszprém, H-8201 Veszprém, Hungary

<sup>c</sup> Department of Physical Chemistry, University of Veszprém, H-8201 Veszprém, Hungary

<sup>d</sup> PPC Technical Services, P.O. Box 40073, Johannesburg 2022, South Africa

<sup>e</sup> MATTEK, CSIR, P.O. Box 395, Pretoria 0001, South Africa

Received 3 April 1998; accepted 27 June 1998

## Abstract

In this paper, results obtained by surface analysis (Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS)) studies performed on the passive layers that formed spontaneously on duplex stainless steels (DSSs) and Ru containing (0.3%) duplex stainless steel (DSS:Ru) in HCl and H<sub>2</sub>SO<sub>4</sub> solutions are presented in order to explain the roles of the different alloying elements in the passivation process. From the AES studies, it followed that the Cr concentrations were slightly higher (about 3%) in the passive layers of both materials, compared to their bulk concentrations, whereas the Ni concentrations were reduced to less than half their bulk concentrations at the outer surfaces of the passive layers, with an increasing concentration gradient towards the bulk of the material. Enrichment of Mo at outer surface of the passive layer was only observed in the case of the DSS:Ru samples which were passivated in HCl. The XPS results indicated that the passive layer on the DSS:Ru samples contained more Cr<sub>2</sub>O<sub>3</sub> and Fe<sup>2+</sup> than Cr(OH)<sub>3</sub> and Fe<sup>3+</sup>, respectively, in the passive layer, compared to the DSS samples without Ru. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Corrosion; Stainless steel; Ruthenium; Surface passivation

## 1. Introduction

Some stainless steel alloys that contain additions of platinum-group metals (PGMs) have a remarkable corrosion resistance in non-oxidizing media ([1–6] and Refs. therein). The introduction of active cathodes into the alloy (cathodic modification) results in

a lowering of the hydrogen over-potential. Thus, the addition of sufficient quantities of PGMs can increase the ability of the alloy to passivate spontaneously. Although several investigations have been carried out on the corrosion behaviour of cathodically modified ferritic and austenitic stainless steels in reducing acids, very little is known about the behaviour of duplex stainless steels in such media.

Duplex stainless steels (DSSs), which are neither austenite nor ferrite, consist of two phases, having a

\* Corresponding author. Tel.: +27-12-420-3508; Fax: +27-12-362-5288; E-mail: gmyburg@scientia.up.ac.za

dispersion of fcc austenite in a matrix of bcc ferrite due to the fact that DSSs contain insufficient amounts of Ni to make them fully austenitic. In general, the DSSs have basic properties which make them very attractive, such as: high strength (approximately twice the tensile strength of austenitic SS), non-hardenable by heat treatment, generally similar or superior mechanical properties than austenitic and ferritic SS, which include weldability and strength and excellent corrosion resistance (better or equivalent to austenitic SS), specially in oxidizing media and conditions conducive to localised corrosion.

The results presented in this paper are the consequences of a joint research project where experiments were carried out to investigate the complex features of the passivation phenomena of DSSs with and without Ru as a minor alloying component (up to 0.3% by mass) in sulphuric and hydrochloric acids. This paper deals more specifically with the surface analytical characterisation of the passive layers formed upon spontaneous passivation on two experimental duplex stainless steels.

Our previous results [7–11], which included several independent techniques such as mass loss tests [7,8], potentiodynamic responses [7,8], in situ radiotracer and ICP methods [8–11], have revealed that the experimental DSSs used in these studies exhibit an enhanced corrosion resistance in HCl and H<sub>2</sub>SO<sub>4</sub> solutions, compared to ordinary austenitic and ferritic grades. Small ruthenium additions can significantly increase the corrosion resistance of the duplex steels, displacing their open-circuit corrosion potentials towards more positive values in the two above-mentioned reducing acid media. In addition, reduced corrosion and critical current densities in both solutions indicate that the ruthenium content inhibits the anodic dissolution of the cathodically modified alloys.

Moreover, in situ radiotracer studies [8–11] have demonstrated that the spontaneous passivation of DSSs with and without Ru in dilute HCl and H<sub>2</sub>SO<sub>4</sub> solutions are influenced by a pronounced sorption of bisulphate/sulphate and chloride ions. Specifically, accumulation of Cl<sup>-</sup> ions on DSSs was found to be small (less than  $1 \times 10^{-10}$  mol cm<sup>-2</sup>) and their irreversible embedding into the surface oxide layer could be ruled out. The surface excess of bisulphate/sulphate ions was considerably higher (up to

$4.5 \times 10^{-10}$  mol cm<sup>-2</sup>), as well as their interaction with passive oxide layers seemed to be substantially stronger than those of Cl<sup>-</sup> ions. The ruthenium content did not exert significant effects on the sorption behaviours of Cl<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ions on the surfaces of the DSSs in either type of acid solutions. The latter statement was supported by the apparently small rate of the dissolution processes as determined by ICP Optical Emission Spectrometry (ICP-OES) [8–10], giving an indication that redistribution of the main alloying elements of the surface passive layers are presumably modest in the course of the spontaneous transformation of duplex steel surfaces.

In light of the antecedents outlined above, this paper will concentrate specifically on some new findings obtained by surface analysis (Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS)) studies of the passive layers that formed spontaneously on experimental DSSs containing Ru (0 or 0.3%) in HCl and H<sub>2</sub>SO<sub>4</sub> solutions in order to understand the role of the different elements in the whole passivation process better.

## 2. Experimental details

The chemical analyses of the experimental DSSs used in this investigation are shown in Table 1. Further information regarding the fabrication of the alloys used in this study is available elsewhere [7].

The compositions of the passive films formed on these DSSs, which spontaneously passivate in HCl and H<sub>2</sub>SO<sub>4</sub>, were studied by AES and XPS. The following sulphuric and hydrochloric acid concentrations were used: 0.1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub>.

The experiments were performed under a constant flow of N<sub>2</sub> gas at 25°C. Spontaneous passivation was carried out after cathodic reduction at -0.8 V (measured against a SCE) for 5 min. After passivation the samples were rinsed in DI water, blow dry with N<sub>2</sub> and then loaded into the spectrometer(s).

The AES studies were conducted in a PHI 610 instrument, operating at 10 keV, while the sputtering was conducted with 3 keV Ar ions, at a sputter rate of about 1 nm/min. This sputtering rate was determined on a Ta<sub>2</sub>O<sub>3</sub> layer. The XPS instrument utilised was a PHI 5300. An Al K<sub>α</sub> radiation with energy of

Table 1  
Chemical composition of the experimental duplex stainless steel studied

Alloy	Elements <sup>a</sup>												
	Fe	Cr	Ni	Mo	Ru	Mn	Si	S	P	O	N	C	
Fe–22% Cr–9% Ni–3% Mo–0% Ru	rest	22.0	9.1	2.8	0.0	0.1	0.07	0.01	0.01	0.02	0.01	0.03	
Fe–22% Cr–9% Ni–3% Mo–0.3% Ru	rest	22.4	9.2	2.9	0.3	0.1	0.03	0.01	0.01	0.04	0.01	0.02	

<sup>a</sup>Percentages by mass.

1486.6 eV was used as primary X-ray source, which was obtained by an acceleration voltage of 15 keV and an emission current of 20 mA. Two different angles (20 and 70°) between the sample surface and the position of the analyser were used to measure the photoelectrons. At low angles, the analyser only detects the photoelectrons coming from the outer most surface, while at larger angles (70°) information from those electrons that are coming from regions deeper inside the surface layer, is also included. In this way, no sputtering is required to obtain depth information and thus eliminates the possibility of sputter-induced modification of the surface layer.

### 3. Results

#### 3.1. AES results

Comparative AES studies were carried out in order to characterise the spontaneous passive films formed on DSSs with and without Ru in HCl and H<sub>2</sub>SO<sub>4</sub>. It should, however, be noted that with AES it is not possible to detect Ru in low concentrations, due to the narrow spacing between the main Ru and C peaks. Fig. 1(a) and (b) show AES depth profiles of DSS containing 0 and 0.3% Ru, respectively, after spontaneous passivation in 1 M H<sub>2</sub>SO<sub>4</sub>. It is obvious from these AES profiles that the Cr is enriched by about 3% in the passive layer compared to the bulk concentration, which is normal for any stainless steel. Ni concentrations were reduced to less than half the bulk concentration at the outer surfaces of the these passive layers, with an increasing concentration gradient towards the bulk of the material. Also visible is an increase in the Ni concentration just below the interface between the sample and the passive layer, as well as a corresponding depletion of Cr in this

region. The concentration of Fe at the outer surface of the passive layer was only about one third that of the bulk concentration. If we compare the depth profiles, it is clear that the Cr concentration in the passive layer of the DSS:Ru is a bit higher compared to the case of the 0% Ru sample, while slightly more Ni is also present at the interface of the 0.3% Ru sample. Also seen in Fig. 1 is the deeper penetration

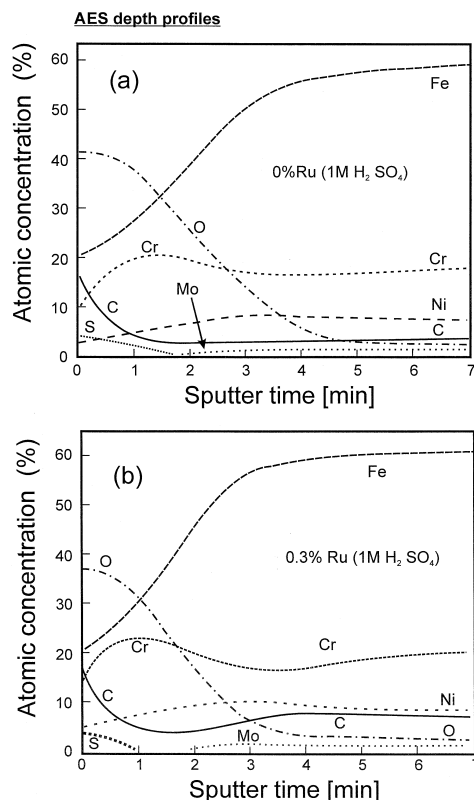


Fig. 1. AES depth profiles of duplex stainless steels (DSS) containing 0% Ru (a) and 0.3% Ru (b), passivated spontaneously in 1 M H<sub>2</sub>SO<sub>4</sub>.

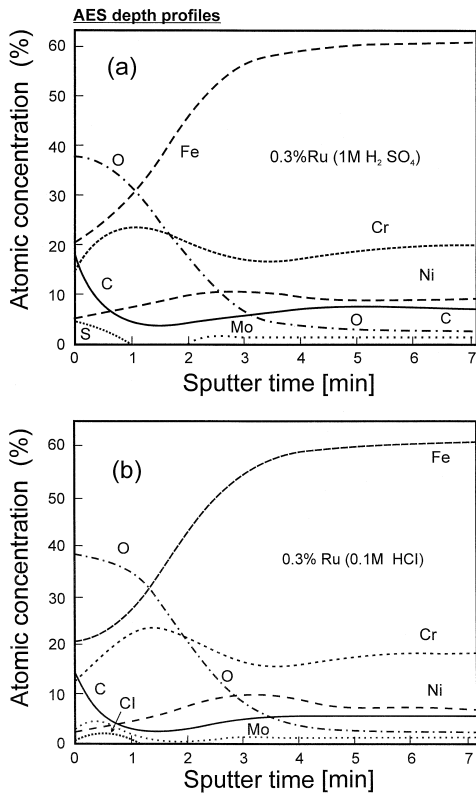


Fig. 2. AES depth profiles of duplex stainless steels containing 0.3% Ru passivated spontaneously in 0.1 M HCl.

of the sulphur into the 0% Ru DSS passivation layer. If the AES depth profile of the DSS:Ru samples passivated in HCl (Fig. 2(b)) is compared with those passivated in H<sub>2</sub>SO<sub>4</sub> (Fig. 1(b)), it is immediately evident that Mo enrichment took place in the passive layer in the former case and might most likely be due to the fact that HCl is a much more aggressive acid.

### 3.2. XPS results

Spectra measured at 20° reflect the situation at the outer most surface of the passive layer, with little contribution from the DSS below the passivation layer, while the 70° spectra contain information from deeper into the sample and therefore not just only of the passivation layer but also of the underlying DSS material. The XPS results shown in Figs. 3–5 for the different elements and angles are representative, irre-

spective whether the samples were passivated in H<sub>2</sub>SO<sub>4</sub> or HCl. When the compound peaks are deconvoluted into different possible peaks, it is possible to determine the contribution of each chemical state of the element under investigation. The energy peak values of the respective XPS peaks were shifted with respect to the C peak at 284.7-eV binding energy. Note that the experimental curves obtained for each element were smoothed before the fittings were performed. The different parameters were kept constant for each respective compound peak throughout the fitting process. In doing this for the Cr peaks obtained from the samples containing 0.3% Ru, it was found (Fig. 3(a) and (b)) that Cr(OH)<sub>3</sub> is the most prominent on the outer surface (measurement at 20°), while at 70°, the Cr<sub>2</sub>O<sub>3</sub> is the predominant contributor to the Cr peaks. The metallic Cr peak is also larger due to the fact that the signals are coming from the passive layer as well as the sample itself (Fig. 3(b)).

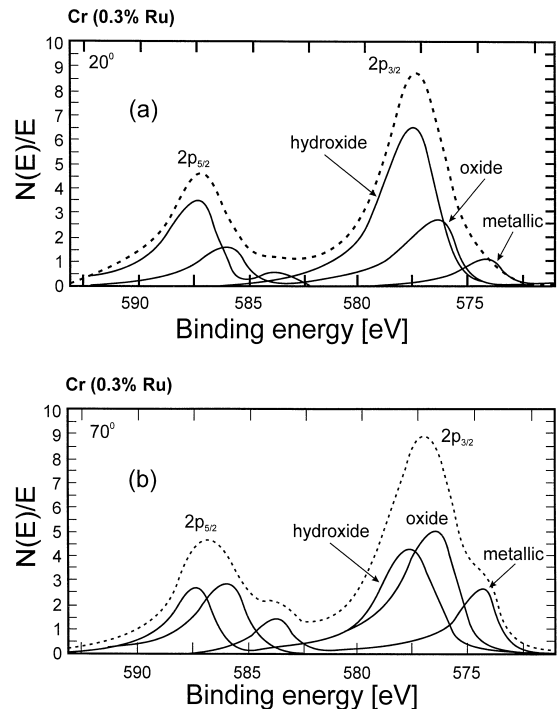


Fig. 3. Cr XPS peaks measured at (a) 20° and (b) 70° angles, respectively, for DSS containing 0.3% Ru and which was passivated spontaneously in 1 M H<sub>2</sub>SO<sub>4</sub>.

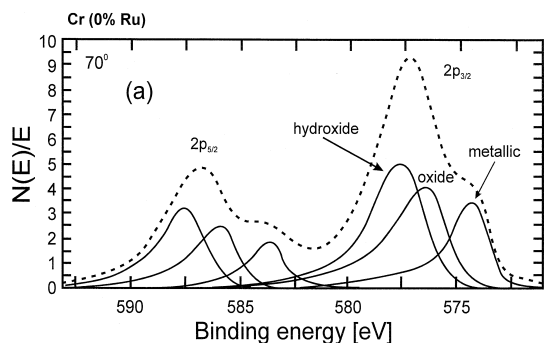


Fig. 4. Cr XPS peaks obtained from DSS containing 0% Ru. XPS peaks were measured at 70° after spontaneous passivation in 1 M H<sub>2</sub>SO<sub>4</sub>.

If we now compare the Cr peaks of the 0% Ru DSS with that of the DSS:Ru sample (Figs. 4 and 3(b)), the Cr (OH)<sub>3</sub> peak in the former case is significantly higher compared to that of the samples containing Ru, whereas the Cr<sub>2</sub>O<sub>3</sub> peak is the high-

est of the three chromium peaks for the 0.3% Ru DSS. These observations were consistent, irrespective of the angles or the acids used. The resistance (passivity) of Cr based stainless steel against chemical attacks is mainly due to the formation and enrichment of Cr<sub>2</sub>O<sub>3</sub> in the passive layer. It seems therefore that the passive layer of the Ru containing DSS is a more effective passive layer due to the increased Cr<sub>2</sub>O<sub>3</sub> content. Furthermore, the presence of Cr(OH)<sub>3</sub> is degrading the effectiveness of the passive layer. These implications are also reflected in the O peaks (Fig. 5(a) and (b)). The O<sub>2</sub><sup>-</sup> peak is slightly higher for the DSS:Ru, if compared to the 0% Ru containing material.

From Fig. 6, it is clear that the Fe<sup>2+</sup> ferric oxide peak is much more enhanced on the DSS:Ru surface than with respect to the 0% Ru DSS material. Note that FeO cannot exist on its own, but is actually part of Fe<sub>2</sub>O<sub>3</sub> which exists as a combination of Fe<sub>2</sub>O<sub>3</sub>

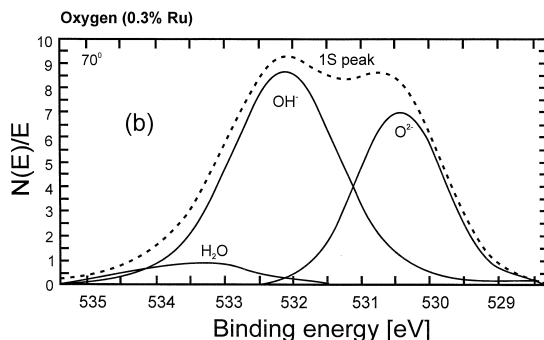
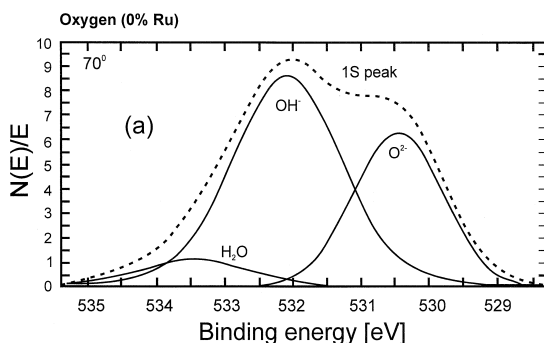


Fig. 5. O XPS peaks obtained from DSS containing 0% Ru (a) and 0.3% Ru (b), respectively. Both these sets of XPS peaks were measured at 70° after spontaneous passivation in 1 M H<sub>2</sub>SO<sub>4</sub>.

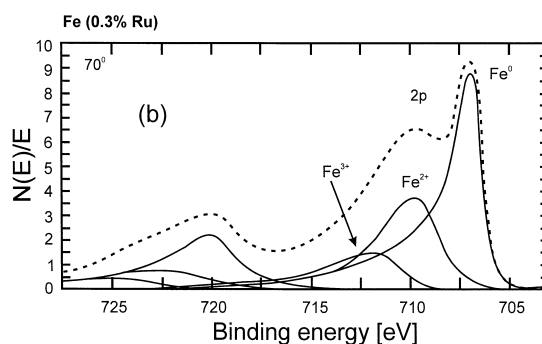
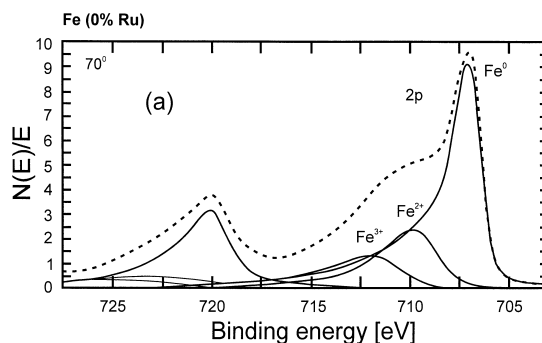


Fig. 6. Fe XPS peaks obtained from DSS containing 0% Ru (a) and 0.3% Ru (b), respectively. Both these sets of XPS peaks were measured at 70° after spontaneous passivation in 1 M H<sub>2</sub>SO<sub>4</sub>.

and FeO. The  $\text{Fe}^{3+}$  peak can be related either to the  $\text{Fe}_2\text{O}_3$  or ferric hydroxide  $\text{FeO}(\text{OH})$ . The energy values of the  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}(\text{OH})$  XPS peaks do not differ much. It cannot be ruled out that both are present, but during the fitting procedure it was not possible to use both in order to simulate the experimental data. The fitted peak energy was taken between the binding energies of  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}(\text{OH})$ . Probably, the enhancement of 'FeO' ferrous oxide and  $\text{Fe}_2\text{O}_3$  in the passive layer is also a factor that helps to increase the passivity of the Ru containing samples.

The Mo XPS peaks were very difficult to fit, not only because they have a very narrow multiplet, but also because of the low concentrations of Mo in the surface layers of the HCl passivated samples. As a result, we are unable to make conclusive remarks regarding the presence and oxidation state of Mo.

As it has been noticed earlier, the Ru and the C XPS peaks are very close to each other. Moreover, owing to the fact that the Ru is present in such a low concentration, it is also impossible to comment positively on the possible chemical state of Ru in the passive layer of these DSSs. Previous investigations [5] by another group indicate that ruthenium can be included in the composition of the passive film as hydroxides and oxides. In the case of Ni, only metallic Ni could be detected.

#### 4. Discussion

Our previous studies [7–11] demonstrate that duplex stainless steels used in the present study have a remarkable corrosion resistance in both HCl and  $\text{H}_2\text{SO}_4$  solutions, irrespectively whether the samples contain Ru as minor alloying element or not. It should, however, be highlighted that the passivation of both duplex stainless steels is most likely due to not only the Ru but the relatively high content of Mo (Table 1). It is assumed that Mo not only retards anodic dissolution, but also increases the effectiveness of the cathodic process owing to the reduced overvoltage of hydrogen on molybdenum [[2] and Refs. therein]. Also, the in situ radiotracer results [8–11] indicate that the ruthenium content does not exert significant effects on the sorption behaviours of  $\text{Cl}^-$  and  $\text{HSO}_4^-/\text{SO}_4^{2-}$  ions on the surfaces of both

duplex stainless steels in either type of acid solutions. This can be related to the fact that the extent of the accumulation of aggressive anions decisively depends on the structure and probably composition of the passive layers. Furthermore, the similarities observed both in the sorption properties and in the dissolution behaviour detected by the ICP-OES method [8–10], provides indirect evidence that redistribution of the main alloying components of the surface passive layers formed on both DSSs, did not differ dramatically from each other.

In general, the dissolution rate of Fe and Cr is higher than that of the alloying elements such as Ni, Mo and Ru [8–10]. Therefore, during the dissolution process these latter alloying elements will be exposed much easier on the surface of the DSS. Of these three elements, we only have evidence that Mo became oxidized and is incorporated in the passive layer. It was also shown with AES that Ni is accumulated just underneath the passive layer. This is in line with previous observations made by Olefjord and Elfstrom [12,13] on austenitic stainless steel, where it is claimed that the Ni accumulation enhances the formation of the passivation layer. It seems therefore that it is also the case with DSS. However, due to the low concentration, Ru could not be observed by AES or XPS. In contrast, our electrochemical measurements [7,8] have revealed an increase in the corrosion potential towards more positive values with an increase in the Ru concentration. This can be considered to be an indication that the surface becomes chemically more stable with an increase in the Ru content. Thus, the surface must be influenced, presumably enriched by Ru. It was shown by Tjong [3] that Ru is enriched on Fe–40 Cr, which contained 0.1 to 0.2 wt% Ru after passivation in 0.5 M HCl. According to Tomashov et al. [4,5], Ru atoms can block lattice point defects and thereby decrease the dissolution rate of Cr. In the case of the DSSs used in this study, it is claimed that both Ni and Ru are acting as blocking elements in order to decrease the dissolution rate of Cr and Fe, while Mo plays an active role by being part of the passive layer. The decrease in the decomposition rate increases the possibility for Cr and Fe to form stable oxides, and in such a way a much more effective passivation layer is formed. The spontaneous formation of the passive layers with excellent corrosion

resistance is apparently initiated by the presence of Mo and Ru, which forces the passivation potential to more positive values and therefore also decreases the dissolution rates of Cr and Fe.

From the considerations outlined above, it is evident that the AES and XPS data are consistent with the in situ radiotracer and ICP-OES results presented in Refs. [8–11], which provided further evidence of the enhanced corrosion resistance of both duplex steels studied.

## 5. Summary

The AES studies indicated that the Cr concentrations were slightly higher (about 3%) in the passive layers of both materials, compared to the bulk concentration, whereas the Ni concentrations were reduced to less than half the bulk concentration at the outer surfaces of these passive layers, with an increasing concentration gradient towards the bulk of the material. Enrichment of Mo was only observed in the case of the DSS samples which were passivated in HCl. The XPS studies showed that the  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  were present in higher concentrations in the Ru contained samples, than in the normal DSS which contained no Ru. These observations correlate with the fact that Ru and Ni act as blocking agents, which decrease the dissolution rates of Cr and Fe, and therefore increase the probability to form a stable passive layer.

## Acknowledgements

MINTEK, FRD (both South African) and the Hungarian Science Foundation (OTKA Grand No. F 4002) and the Ministry of Education (ANFK Grant No. 550/92) are acknowledged for supplying the alloys and funding used in this investigation.

## References

- [1] J.H. Potgieter, A.M. Heyns, W. Skinner, *J. Appl. Electrochem.* 20 (1990) 7112.
- [2] J.H. Potgieter, *J. Appl. Electrochem.* 21 (1991) 471 or 971.
- [3] S.C. Tjong, *Appl. Surf. Sci.* 45 (1990) 301.
- [4] N.D. Tomashov, G.P. Chernova, E.N. Ustinsky, *Corrosion* 40 (1984) 134.
- [5] N.D. Tamashov, G.P. Chernova, L.A. Chigirinskaya, E.A. Nasedkina, *Prot. Met.* 22 (1986) 704.
- [6] K. Varga, P. Baradlai, W.O. Barnard, G. Myburg, P. Halmos, J.H. Potgieter, *Electrochem. Acta* 42 (1997) 25.
- [7] J.H. Potgieter, W. Skinner, A.M. Heyns, in: *Proceedings of the 1st International Chromium Steel and Alloys Congress*, 2, 1992, p. 235.
- [8] J.H. Potgieter, W.O. Barnard, G. Myburg, K. Varga, P. Baradlai, L. Tomcsányi, *J. Appl. Electrochem.* 26 (1996) 1103.
- [9] K. Varga, P. Baradlai, W.O. Barnard, J.H. Potgieter, P. Halmos, *Magy. Kém. Folyóirat* 102 (1996) 143.
- [10] P. Baradlai, K. Varga, W.O. Barnard, J.H. Potgieter, *Korróziós Figyelő* 35 (1995) 97.
- [11] P. Baradlai, J.H. Potgieter, W.O. Barnard, L. Tomcsányi, K. Varga, *Mater. Sci. Forum* 185–188 (1995) 759.
- [12] I. Olefjord, B.O. Elfstrom, *Corrosion* 38 (1982) 46.
- [13] I. Olefjord, B. Brox, U. Jelvestam, *J. Electrochem. Soc.* 132 (1985) 2854.