# Study of the Corrosion of Steel Superduplex UNS S32750 Involving Different Ferrite / Austenite Ratio in Acid Solutions Containing Chloride

Rodrigo R. A. Garcia and Oscar R. Mattos

Laboratório de Ensaios Não Destrutivos, Corrosão e Soldagem – LNDC, COPPE Universidade Federal do Rio de Janeiro – UFRJ, Cx. Postal 68505, CEP 21945-970, Rio de Janeiro, RJ, Brazil rodrigo\_garc@metalmat.ufrj.br

### Introduction

Duplex stainless steels and super duplex are dual alloys with ferrite and austenite phases. They provide an excellent corrosion resistance in a wide variety of media. The UNS S32750 alloy is mainly used under severe conditions and can replace austenitic stainless steels in many applications. These alloys usually present better corrosion resistance than the austenitic steels, besides having higher mechanical strength and toughness. The use of duplex and super duplex steels therefore can turn them into an excellent choice of steel for many specific applications. In this work, the electrochemical dissolution of alloy UNS S32750 with different ferrite / austenite ratio, immersed in HCl – H<sub>2</sub>SO<sub>4</sub> and NaCl – HCl solutions was studied. The influence of the ferrite / austenite ratio on the electrochemical characteristics of these alloys was then investigated. The experimental was based on potenciodynamic polarization, measurements of open circuit potential, electrochemical impedance spectroscopy (EIS) and tests of mass loss. By these tests it was concluded that, as the solubility temperature (T<sub>solub</sub>) increases in the temperature range of 1120 to 1300 ° C, the overall corrosion of the alloy increases as well. Additionally, the effect of pH and the chloride content of the electrochemical dissolution of the alloys were studied.

### Experimental

Samples were cut as small sheets from a cross section of a commercial superduplex pipe (6 inch) (UNS S32750). The prepared sample sheets had rectangular dimensions of 1 cm x 1.2 cm, with approximately 1cm of thickness and were embedded in an epoxy resin in view to expose only one side. Different samples were prepared with an area of about 10 cm<sup>2</sup>, with a small hole for a passing a Nylon® thread in order to keep the specimen hung into solution. In these samples, heat treatments were performed at three different temperatures for 1h and cooled rapidly in water, obtaining the  $\delta$ : $\gamma$  ratio shown in table I.

Table I.						
Annealing Temperature ( <sup>o</sup> C)	%δ	%γ	δ:γ			
1120	0.56	0.44	1.3			
1220	0.61	0.39	1.6			
1300	0.65	0.35	1.9			

The electrolytes studied can be summarized into two major groups. They were all kept at room temperature with no special air sealing systems for the experiments.

- 1. Solutions HCl-H<sub>2</sub>SO<sub>4</sub>, these solutions were used to change the pH maintaining the chloride concentration in 3M and 1M. The electrolytes used are shown in Table II.
- 2. Solutions 3M NaCl 3M HCl, these solutions were used to change the pH but maintaining the chloride concentration constant equal to 3M. Table III

### **Results and Discussion**

Potentiodynamic polarization results are given in Table II. The influence of the  $Cl^-$  was analyzed using a scan rate of 0.56 mV / s and applying a overvoltage of 0.7 V starting at the open circuit potential ( OCP). Only the current density associated with the active/transition is shown in the table.

Table II. Solutions mixing HCl and H2SO <sub>4</sub> . Sample annealed at 1300 °C										
Electrolyte		$[\mathrm{H}^+]$	$[Cl^{-}]$	i(active/passive)	Electrolyte		$[\mathrm{H}^+]$	[Cl <sup>-</sup>	i(active/passive)	
		/ M	/ M	$(mA/cm^2)$			/ M	] /	$(mA/cm^2)$	
								Μ		
1	3M HCl	3	3	2.820	4	1M HCl	2	1	0.830	
						+ 1M				
						$H_2SO_4$				
2	3M HCl	4	3	10.900	5	1,5M	2	1,5	1.127	
	+ 1M					HCl +				
	$H_2SO_4$					0,5M				
3	3M HCl	6	3	114.00		$H_2SO_4$				
	+ 3M									
	$H_2SO_4$									

From Table II is possible to note that the transition active/passive is more affected by the pH than by the chloride. Indeed, comparing the current densities obtained with electrolytes 4 and 5 ([ $H^+$ ] =2M) with the respective values for the electrolytes 1-3 is possible to see that pH is more important than the chloride to fix the activity of the steel. The next results show that the concentrations of chloride were maintained at 3M while the pH was changed.

Figure 1 presents the EIS results obtained for 1300  $^{\circ}$ C solubilized sample after 5h of total immersion time. The electrolyte used are seen in Table III

Electrolyte	% HCl	% NaCl	Electrolyte	% HCl	% NaCl
	(3M)	(3M)		(3M)	(3M)
6	0	100	10	14	86
7	6	94	11	20	80
8	7	93	12	100	0
9	8	92			



Figure 1. Nyquist diagram of the sample solubilized in 1300  $^{\circ}$  C in 8% HCl (3M) + 92% NaCl (3M), with 5 hours of total immersion.

Nyquist diagrams were obtained for immersion times of 7 h, 31 h, and 55 h for this sample immersed in each electrolyte presented in Table III. The same procedure was performed in solubilized samples at 1120 °C and 1220 °C. It was found that decreasing the pH (increasing the concentration of HCl) causes a decrease in both of R<sub>1</sub> as R<sub>p</sub>. In tests with a concentration of 20% HCl (3M) in relation to the volume of NaCl (3M), only one capacitive loop and one inductive arc are present. Tests with lower concentrations tend to present two capacitive and one inductive loop. A curious result is that the capacitance of the first capacitive loop  $(C_1)$ was always between 2.3 and 35.9 mF and showed that their values increase with the decrease of the pH. For those tests after more than 24 hours of immersion, the electrode surface was covered with a corrosion product (a dark, non-adherent, porous, high surface roughness product), and the impedance presents a linear behavior in high frequency region. Such behavior was associated with the porosity of this layer. Another result was that the higher the annealing samples temperatures, the lower the values  $R_1$  and  $R_p$ . These impedance results were compared with results of mass loss tests according to ASTM G31 and ASTM G1. It was shown that there was a correlation, both for  $R_1$  and  $R_p$  with the weight loss. But the factor of proportionality was different for each different temperature. Optical microscopy results confirmed that the austenite phase remains practically immune, while the ferrite phase is preferably corroded. This result indicates that the main reason for the higher mass loss of those samples solubilized at higher temperatures was the increased formation of ferrite, that was the phase majorly degraded.

## Conclusion

After the results of potentiodynamic polarization, EIS, metallographic analysis and mass loss tests on samples solubilized by different heat treatments have reached the following conclusions in this work:

The effect of Cl<sup>-</sup> in the anodic dissolution of this class of steel is not as severe as the pH. The preferential attack of ferrite was the main process detected in the dissolution. The capacitance values obtained are extremely high, comparable to those of super capacitors. The capacitance of a sample at a given temperature, immersed in HCl (3M) - NaCl (3M), increases with time . A relationship exists between the mass loss and both the values of R<sub>1</sub> and R<sub>p</sub>.

#### Acknowledgements

The authors would like to thank Capes and CNPq for the financial support on this work.

### References

 SYMNIOTIS, E. 1995. Dissolution Mechanism of DDS in the Active-to-Passive Transition Range and the Role of Microstructure. Corrosion Science. 1995, Vol. 51, 8, p. 10.
TSAU, WEN-TA e CHEN, JHEN-RONG. 2007. Galvanic corrosion between the constituent phases in duplex stainless steel. Corrosion Science. 2007, Vol. 49, pp. 3659–3668.
D.S. CARVALHO, C.J.B. JOIA, O.R. MATTOS. 2005. Corrosion rate of iron and iron– chromium alloys in CO<sub>2</sub> medium. Corrosion Science. 2005, Vol. 47, pp. 2974–2986.