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Effect of Cyclic Heat Treatment Process on the Localized Corrosion Resistance of 409 Ferritic, 430 Ferritic, 3163 Austenitic and 444 Ferritic Stainless Steels for High Temperature Applications

Roland T. Loto¹

¹Department of Mechanical Engineering, Covenant University, Ogun state, Nigeria

tolu.loto@gmail.com

Abstract. The corrosion resistance of as-received 409 ferritic, 430 ferritic, 444 ferritic and 316 austenitic stainless steels was studied in 0.05M $H_2SO_4/3.5\%$ NaCl solution by potentiodynamic polarization and potentiostatic measurement and compared to their counterparts subjected to repetitive temperature variation at 1000°C. As-received 409 ferritic steel exhibited the highest corrosion rate at 8.406 mm/y compared to as-received 316 austenitic steel with the lowest corrosion rate at 3.130 mm/y. Corrosion rate of heat treated 409, 430 and 444 ferritic stainless steels significantly increased to 10.766 mm/y, 5.694 mm/y and 6.096mm/y while the corrosion rate of as-received 316 austenitic steel decreased to 0.409 mm/y. As-received 444 ferritic steel exhibited the weakest resistance to pitting corrosion while as-received 409 ferritic steel exhibited the most significant metastable pitting activity. Pitting corrosion susceptibility of heat treated 409 ferritic, 316 austenitic and 444 ferritic steel decreased significantly to 0.137 V, 0.384 V and 0.096 V while heat treated 430 ferritic steel exhibited significant improvement in pitting corrosion resistance.

1. Introduction

Vehicular exhaust system is made up of piping linkages responsible for the transport of hot reaction fluids from the combustion section of the engine to the exhaust manifold and through the exhaust muffler to the tail end of the exhaust pipe [1]. Corrosion of the exhaust system results in breakdown of the metallic parts causing leakage of internal parts, components, vibration, air pollution and noise issues. The operating conditions of exhaust systems in addition to liquefied corrosive ions in the exhaust fluid requires strong precautions in material selection for the manufacture of exhaust system parts and components to ensure optimum performance and long operating lifespan. Stainless steels are used in the manufacture of exhaust mufflers due to their proven excellent corrosion resistance, heat resistance and aesthetic properties. However, corrosion constitutes the major problem for the accelerated degradation of exhaust mufflers and other components of the exhaust system leading to loss of operating performance [2]. Carbon steels are mostly used in the manufacture exhaust systems. However, their weak corrosion resistance is responsible for their short operating lifespan. Aluminised carbon steel is more applicable than carbon steel with strong pitting resistance, but is weak under high temperature operating conditions. Specialty stainless steels offer higher performance but are generally costly [3]. 409 ferritic stainless steels has become the conventional replacement for carbon steel grades. However, they have low coefficient of thermal expansion, coarsening at welding temperatures and are susceptible to localized corrosion deteriorations [4]. Some grades of stainless steels are capable of



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withstanding the deteriorating actions of corrosive anions under high temperature. However, there are cases where corrosion resistance of the steel is enhanced, decreases or remain unchanged [5-7]. Previous research on the passive film stability and pitting corrosion of S40900 stainless steel in 0.1 M NaCl and chloride/sulphate solutions show the passive film presents n-type semi conductive behavior with grain boundaries playing an important role as pitting initiation sites. Results also showed S40900 corrosion rate is proportional to the concentration of SO_4^{2-} and Cl^- anions in the electrolyte [8, 9]. 304L steel showed no passivation and resistance to pitting after 0% NaCl concentration coupled with increase in corrosion rate [10]. This research focuses on the effect of repetitive high temperature conditions on the corrosion resistance of 430 ferritic, 444 ferritic and 316 austenitic stainless steel in sulphate-chloride solution in comparison to the corrosion resistance of the conventional 409 ferritic stainless steels.

2. Material and Methods

As-received 409 ferritic stainless steel (409AS) was sourced from a vehicle exhaust muffler. 430 ferritic stainless steel (430AS), 316 austenitic stainless steel (316AS) and 444 ferritic stainless steel (444AS) were sourced from Vienna, Austria. The elemental compositions of the steels were confirmed with PhenomWorld scanning electron microscope (Model No. MVE0224651193). One test for each stainless steel specimen were cut and mounted in resin mounts with visible surface areas of 1 cm² after which the exposed surfaces of the steels were metallographically prepared. 800 mL of 0.05 M H₂SO₄ solution at 3.5% NaCl concentration was formulated from standard grade concentration of the acid (98% purity) and NaCl (recrystallized). A second set of prepared stainless steel specimens (409HT, 430HT, 316HT and 444HT) were subjected to heat treatment within a muffle furnace at 1000°C for 30 minutes and subsequently cooled to room temperature. Electrochemical test of 409AT, 430AT, 316AT and 444AT stainless steels was done with Digi-Ivy potentiostat at 30 °C ambient temperatures interfaced with a computer. Polarization curves were plotted at scan rate of 0.0015 V/s from -1.5 V to +1.5 V.

3. Results and discussion

3.1 Potentiodynamic polarization studies

Potentiodynamic polarization data for as-received and heat treated stainless steel corrosion in 0.05M H₂SO₄/3.5% NaCl concentration are shown in table 1. 409AS exhibited the highest corrosion rate value of 8.406 mm/y among the as-received steels while 316AS had the lowest corrosion rate at 1.581 mm/y. 444AS and 430AS showed less susceptibility to H_2 embrittlement from observation of its cathodic Tafel slope. The relatively high anodic Tafel slope of 430ST confirms it is susceptibility to anodic degradation. Data for cathodic Tafel slopes of the as-received steel shows the reduction mechanisms is under activation control. However, the anodic reaction mechanisms control the redox reaction mechanism based on the anodic Tafel slope values. Heat treatment significantly increased the corrosion resistance of the alloy specimens. 409HT exhibited a corrosion rate value of 10.766 mm/y. Corrosion rate of 430HT and 444HT increased to 5.694 mm/y and 6.096 mm/y. Difference in corrosion potential and corrosion rate between the as-received and heat treated 430 ferritic steel confirms the deteriorating effect of heat treatment. The corrosion potential difference between asreceived and heat treated 409 and 444 ferritic steels from -0.499 V and -0.454 V to -0.502 V coupled in addition to increased corrosion rate also shows heat treatment enhances the initiation and growth of localized corrosion reactions. Heat treatment increased the corrosion resistance of 316 austenitic steel from 1.581 mm/y to 0.490 mm/y while its corrosion potential shifted from -0.411 V to -0.323 V.

A-recei	ved Steels							
	Corrosion	Corrosion	Corrosion	Corrosion	Polarization	Cathodic	Anodic	
	Rate	Current	Current	Potential	Resistance,	Potential,	Potential,	
Steel	(mm/y)	(A)	Density (A/cm ²)	(V)	$R_{ m p}\left(\Omega ight)$	$B_{\rm c}$ (V/dec)	$B_{\rm a}$ (V/dec)	
409ST	8.406	7.82E-04	7.82E-04	-0.499	32.8	-6.109	-1.211	
430ST	3.504	3.26E-04	3.26E-04	-0.502	78.8	-6.445	4.976	
316ST	1.581	1.51E-04	1.51E-04	-0.411	170.1	-6.060	7.317	
444ST	3.130	2.95E-04	2.95E-04	-0.454	87.1	-6.250	4.550	
Heat Treated Steels								
	Corrosion	Corrosion	Corrosion	Corrosion	Polarization	Cathodic	Anodic	
	Rate	Current	Current	Potential	Resistance,	Potential,	Potential,	
Steel	(mm/y)	(A)	Density (A/cm ²)	(V)	$R_{ m p}\left(\Omega ight)$	$B_{\rm c}({\rm V/dec})$	B _a (V/dec)	
409ST	10.766	1.00E-03	1.00E-03	-0.502	25.6	-6.798	-1.193	
430ST	5.694	5.30E-04	5.30E-04	-0.463	48.5	-6.537	1.050	
316ST	0.490	4.68E-05	4.68E-05	-0.323	1169.0	-7.535	11.070	
111ST	6.096	5 75F-04	5 75E-04	-0 502	44 7	-6 008	0.252	

Table 1. Polarization data for as-received and heat-treated 409 ferritic, 430 ferritic, 316 austeniticand 444 ferritic stainless steel corrosion in 0.05 M H2SO4/3.5% NaCl solution.

3.2 Potentiostatic studies

The metastable pitting and stable pitting graphical portions for as-received and heat treated 409 ferritic, 430 ferritic, 316 austenitic and 444 ferritic steel are shown from figure 1(a) to figure 2(b). Table 2 shows the potentiostatic data of the steels obtained. 409AS displayed the widest metastable pitting portion for the as-received steels [11]. The metastable pitting current of 409AS at onset is 2.58×10^{-3} A which is greater than the values obtained for 430AS, 316AS and 444AS. 430AS metastable pitting current initiated at 2.14 x 10⁻³ A and passivated at 5.91 x 10⁻⁵ A compared to 409AS which passivated at 2.90 x 10⁻⁵ A. 316AS and 444AS underwent early metastable pitting at 4.68 x 10⁻⁴ A and 3.60 x 10⁻⁴ A, and passivated at 3.97 x 10^{-4} A and 6.10 x 10^{-5} A. The passivation range and pitting potential of 316ST are 0.145 V and -0.031 V due to weak resistance to localized corrosion deterioration. 444AS and 409AS had passivation range values of 0.592 V and 0.296 V, and pitting corrosion potential of 0.087 V and 0.296 V due to strong resistance to localized corrosion compared to 430ST and 409ST. The passivation range of 409HT, 316HT and 444HT (heat treated steels) [table 2] shifted from 0.296 V, 0.145 V and 0.592 V to 0.137 V, 0.384 V and 0.096 V due to decreased resistance to localized corrosion [figure 1(b)]. 444HT is relatively more susceptible to high temperature variation with due to differences in its corrosion rate and visible decrease in passivation plot. Absence of metastable pitting activity on the plot of 316HT in addition to significantly lower corrosion rate shows it is applicable for high temperature application. The steel passivated at -0.210 V (1.68 x 10⁻⁴ A). 430HT exhibited passivation range of 0.384 V making it applicable vehicular mufflers. The short metastable pitting plot of 430HT initiated at 7.88 x10⁻⁴ A and passivated at 1.15 x 10⁻⁴ A is due to resistance to oxidation. The pitting potential values of 409HT, 316HT and 444HT shows decrease to localized corrosion.

As-received Steel										
	Metastable Pitting	Passivation	Passivation	Pitting Potential	Passivation					
Steel	Current (A)	Current (A)	Potential (V)	(V)	Range (V)					
409	2.58E-03	2.90E-05	-0.209	0.087	0.296					
430	2.14E-03	5.91E-05	-0.214	-0.038	0.176					
316	4.68E-04	3.97E-04	-0.176	-0.031	0.145					
444	3.60E-04	6.10E-05	-0.332	0.260	0.592					
Heat Treated Steel										
11	eat Treated Steel									
	Metastable Pitting	Passivation	Passivation	Pitting Potential	Passivation					
Steel	Metastable Pitting Current (A)	Passivation Current (A)	Passivation Potential (V)	Pitting Potential (V)	Passivation Range (V)					
Steel 409	Metastable Pitting Current (A) 3.24E-03	Passivation Current (A) 1.07E-04	Passivation Potential (V) -0.297	Pitting Potential (V) -0.160	Passivation Range (V) 0.137					
Steel 409 430	Metastable Pitting Current (A) 3.24E-03 7.88E-04	Passivation Current (A) 1.07E-04 1.15E-04	Passivation Potential (V) -0.297 -0.326	Pitting Potential (V) -0.160 0.058	Passivation Range (V) 0.137 0.384					
Steel 409 430 316	Metastable Pitting Current (A) 3.24E-03 7.88E-04	Passivation Current (A) 1.07E-04 1.15E-04 1.68E-04	Passivation Potential (V) -0.297 -0.326 -0.210	Pitting Potential (V) -0.160 0.058 -0.174	Passivation Range (V) 0.137 0.384 0.036					

Table 2. Potentiostatic data for untreated and heat treated 409ST, 430ST, 316ST and 444ST corrosion in 0.05 M $H_2SO_4/3.5\%$ NaCl solution.









4. Conclusion

Repetitive temperature variation significantly influenced the corrosion resistance of as received and heat-treated 430 ferritic, 316 austenitic and 444 ferritic stainless steel when compared to the corrosion

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resistance of 409 ferritic steel in chloride-sulphate solution. Corrosion rate of as-received 430 ferritic, 316 austenitic and 444 ferritic steel were significantly lower than the value for as-received 409 ferritic steel. Application of heat treatment processes increased the corrosion rate of the heat-treated stainless steel counterparts with heat-treated 409 ferritic steel having the highest value. As-received 444 ferritic steel exhibited the lowest vulnerability to pitting corrosion compared to as-received 409 steel. The pitting resistance of heat-treated 409 ferritic, 316 austenitic and 444 ferritic were significantly lower than their as-received counterparts while 430 ferritic steel showed significant improvement in pitting corrosion resistance.

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