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MATERIALS ENGINEERING | RESEARCH ARTICLE

Influence of delta ferrite on corrosion susceptibility of AISI 304 austenitic stainless steel

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Abstract: In the current study, the influence of delta (δ) ferrite on the corrosion susceptibility of AISI 304 austenitic stainless steel was evaluated in 1Molar concentration of sulphuric acid (H_2SO_4) and 1Molar concentration of sodium chloride (NaCl). The study was performed at ambient temperature using electrochemical technique—Tafel plots to evaluate the corrosive tendencies of the austenitic stainless steel sample. The as-received (stainless steel) specimen and 60% cold-worked (stainless steel) specimens were isothermally annealed at 1,100°C for 2 h and 1 h, respectively, and quenched in water. The results obtained show that the heat-treated specimen and the 60% cold-worked plus heat-treated specimen exhibited higher corrosion susceptibility than the as-received specimen, which invariably contained the highest fraction of δ ferrite particles. The finding shows that the presence of δ ferrite, in which chromium (Cr), the main corrosion inhibitor segregates, does not degrade and or reduces the resistance to aqueous corrosion of the austenitic stainless steel material.

Subjects: Manufacturing Engineering; Material Science; Materials Science

Keywords: austenitic stainless steel; delta ferrite; corrosion rates; Tafel; polarization resistance



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Lawrence O. Osoba is a lecturer in the Department of Metallurgical and Materials Engineering, University of Lagos, Lagos Nigeria. He is a resourceful Metallurgical and Materials engineer with eight years of practical industry experience in Foundry Technology. Osoba has specialized knowledge in engineering research, involving joining of materials and characterization of the joint properties, aside from skills in quality management, production planning, and process control. His current research focus is in the area of processing—microstructure—property relationship studies in aerospace and composite materials.

Raheem and Ikenna are graduate students in the Department of Metallurgical and Materials Engineering. In this study, detailed experimental procedure with analysis was used to correlate the corrosion behavior with the observed microstructural features in the material to understand better, the influence of delta ferrite on Corrosion Susceptibility of Stainless Steel.

PUBLIC INTEREST STATEMENT

Rust resistance metals such as the popular stainless steel often contain some quantities of delta (δ) ferrite that has been previously reported to lower its strength and ability to withstand repeated load application. This work investigated the role of the delta (δ) ferrite on corrosion susceptibility of stainless steel in sulphuric acid (H_2SO_4) and sodium chloride (NaCl) environment. The results of the study show that the amount of δ -ferrite in a matrix in which chromium (Cr), the main corrosion resistance enabling element dominates, does not reduce or compromise significantly, the rust resistance properties of the stainless steel materials.

1. Introduction

About two-third of the world total production of stainless steel is made of austenitic stainless steel. Austenitic stainless steels production is about 65–70% of the total US stainless steel production and occupied a dominant position because of their high corrosion resistance, strength, and toughness at both elevated and ambient temperatures (Decker, Eash, & Goldman, 1962). In the high temperature treatment of stainless steels, such as encountered in forging and rolling processes, $M_{23}C_6$ and chromium carbide are formed along grain boundaries of austenite, causing preferential depletion of Cr along the grain boundary and consequently increased rate of corrosion (Binder, Brown, & Franks, 1949). The result of this is intergranular corrosion of the sensitized austenitic stainless steel, which are generally insidious. The austenitic stainless steel sometimes appears physically harmless in service, but in reality its corrosion causes severe internal degradation that have deleterious outcome (Warren, 1959). The driving force for sensitization is the difference in corrosion potential that develops between the grain boundary and the bulk material on adjacent grains.

A major requirement for reliable mechanical property of austenitic stainless steel and other alloys is microstructural stability (Janovec, Sustarsic, Medved, & Jenko, 2003), which are often achieved through heat treatment (Plaut, Herrera, Escriba, Rios, & Padilha, 2007). The properties and performance of austenitic stainless steels are strongly related to the texture of δ -ferrite, which, in the case of casting, depends chiefly on chemical composition and on the cooling rate during solidification (Padilha & Rios, 2002). Delta (δ) ferrite is formed during solidification and remains in the microstructure at room temperature. The presence of delta ferrite, which is a strong barrier to the dislocation motion, slows down grain growth, increases strength, and reduces fatigue properties (Astaf'ev, Lepekhina, & Batieva, 1989).

Electrochemical techniques of corrosion measurement are currently gaining attention as corrosion measuring technique, primarily due to the speed of measurement and reliability of results, especially when estimating corrosion rate of highly corrosion resistant metals or alloys. The corrosion rate was calculated from Equation (1) (Xianming & Shizhe, 2005), while the polarization resistant was obtained from Equation (3) (Grauer, Moreland, & Pini, 1982).

$$i = i_{\text{corr}} \exp \frac{2.3(E - E_{\text{corr}})}{\beta a} - \frac{2.3(E - E_{\text{corr}})}{\beta c} \quad (1)$$

where E_{corr} = corrosion potential.

$$B = \frac{\beta a \beta c}{2.3(\beta a + \beta c)} \quad (2)$$

$$R_p = \frac{B}{i_{\text{corr}}} = \frac{(\Delta E)}{(\Delta i)_{\Delta E \rightarrow 0}} \quad (3)$$

where: R_p = polarization resistance, i_{corr} = corrosion current density, and B = empirical polarization reciprocal.

The relationship between B , the anodic (βa), and cathodic (βc) Tafel slopes is given by Equation (2) and the relationship between current density (i_{corr}) and potential (E_{corr}) on the polarization curve is given in Equation (3).

Although information on the presence of δ -ferrite with BCC structure in an FCC austenitic matrix is available in literature (Franks, Binder, & Brown, 1945), but literature on the influence of the δ -ferrite on corrosion susceptibility of stainless steel are few, thus, the need for the current study to investigate the influence of delta ferrite on corrosion susceptibility of AISI 304 austenitic stainless steel in H_2SO_4 and NaCl environments.

Table 1. Spectro analysis results of the austenitic stainless steel

Austenitic stainless steel	Chemical composition, wt.%									
	Fe	C	Si	Mn	P	S	Cr	Ni	N	Cu
Wt.%	66.24	0.0379	0.2865	1.483	>0.117	0.0364	20.95	9.627	0.098	1.058

2. Experimental procedure

2.1. Material and methods

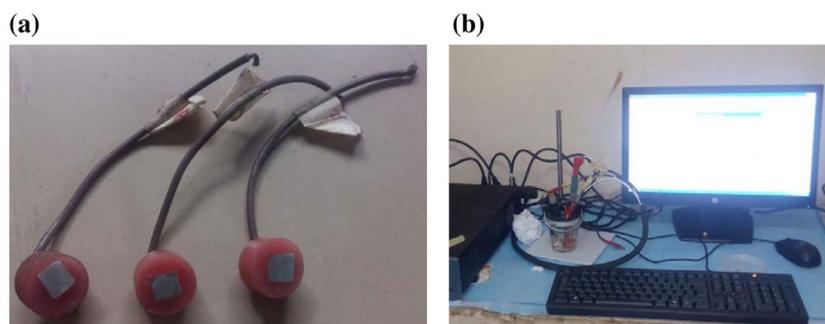
An AISI 304 stainless steel rod, 24-mm diameter and 14-mm long, is used in this study. The chemistry of the stainless steel material given in Table 1 is obtained using an Optical Emission Spectroscopy testing machine (ARL QuantoDesk Spectro Analysis Machine). Heat treatment and rolling of the test specimens were carried out to dissolve the δ -ferrite present in the as-received (stainless steel) specimen. The cold working process was carried out using Buhler precision power plate rolling mill. The austenitic stainless steel samples were drawn by means of friction into the two revolving roll gap. The compressive force applied by the rolls reduces the thickness of the stainless steel sample by 60% from 24 mm to 5.6 mm. The as-received and cold-worked specimens were annealed in a box-type muffle furnace (Figure 1) at 1,100°C for 2 h and 1 h, respectively, and then quenched in water to preserve the high-temperature microstructure.

As-received, heat-treated and the 60% cold-worked plus heat-treated samples were prepared for metallographic observations using SiC impregnated emery papers of 60, 80, 120, 220, 400, 600, 800, 1,000, and 1,200 grit sizes in succession while lubricating with water. Subsequently, the ground samples were mechanically polished using a polishing cloth and a 0.3 micron SiC polishing powder. The specimens were etched by swabbing in a solution of 10% oxalic acid for about 3–4 min in preparation for microscopic examination.

Figure 1. Box-type muffle furnace.



Figure 2. (a) Cold mounted samples as working electrodes and (b) AutoLab PGSTAT 204N instruments.



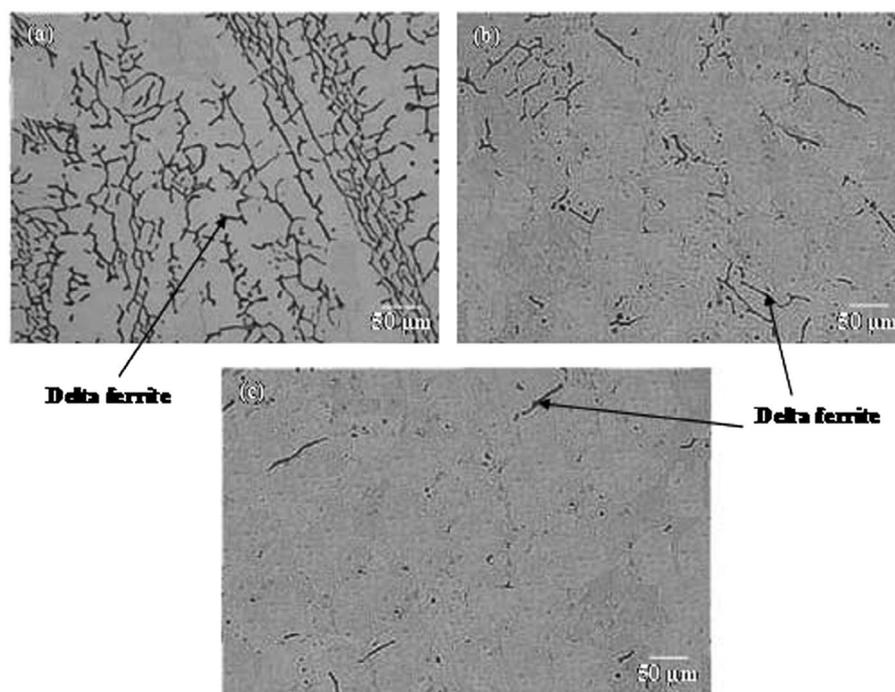
The electrochemical experiments were carried out using AUTOLAB PGSTAT 204N instrument, piloted by NOVA software. The experiments were performed according to ASTM G3-14 (American Society for Testing & Materials G3-14, 2014) at room temperature using a three-electrode corrosion cell setup comprising of austenitic stainless steel as the working electrode (surface area = 10 mm²), saturated silver/silver chloride as reference electrode, and platinum rod as counter electrode (see Figure 2(a) and (b)). The test electrolytes were 1 M sulfuric acid (H₂SO₄) and 1 M sodium chloride (NaCl). The working electrode was immersed in a test solution for 30 min until a stable open circuit potential was attained. The working electrodes were prepared by attaching an insulated copper wire to one face of the sample using an aluminum conducting tape, and cold mounted in resin. Potentiodynamic polarization measurements were carried out at a scan rate of 1.0 mV/s at a potential initiated at -250 to +250 mV. After each experiment, the electrolyte and the test sample was replaced. All corrosion potential measurements recorded in this study were with respect to the saturated calomel electrode.

3. Results and discussion

3.1. Microstructures

In Figure 3(a) the microstructure of the as-received specimen shows the presence of δ -ferrite phase in an austenite matrix. The micrograph is comparable to literature (Gigović-Gekić & Oruč, 2011;

Figure 3. Microstructure of AISI 304 stainless steel: (a) as-received sample (b) as-received heat-treated sample at 1,100°C for 2 h and (c) 60% cold worked and heat treated at 1,100°C for 1 h.



Padilha, Tavares, & Martorano, 2013; Vander Voort, 2013). The microstructure of heat-treated specimen at 1,100°C for 2 h is shown in Figure 3(b). The microstructure showed a qualitative significant reduction in number density of the δ -ferrite content in the austenitic matrix. Micrograph of the specimen cold worked (60% deformation) and heat treated at 1,100°C for 1 h (Figure 3(c)) also revealed a further reduction in the amount of δ -ferrite compared to that observed in the as-received sample. The microstructural variations with heat treatment and non-equilibrium processing that occurred is a confirmation that precipitate dissolution can be enhanced by heat treatment and cold working.

3.2. Electrochemical investigations

The electrochemical technique of polarization resistance was used to measure corrosion rates, expressed in millimeter per year (mm/yr). From the linear Tafel segments of the anodic and cathodic curves, it was possible to determine the corrosion rates of the austenitic stainless steel by extrapolating to obtain the corrosion current densities (I_{corr}) and corrosion potential (E_{corr}). Furthermore, polarization resistance, a measure of the corrosion resistance of a material, can be directly related to its corrosion rate.

3.3. Effect of heat treatment and cold working on corrosion susceptibility in H_2SO_4

Table 2 and Figure 4 show the corrosion reaction data and polarization curves of specimen immersed in 1 M sulfuric acid (H_2SO_4) environment, respectively. In terms of corrosion rate, it is observed that the 60% cold-worked and heat-treated sample had the highest corrosion susceptibility, followed by the sample heat treated at 1,100°C for 2 h while the as-received stainless steel sample showed the least corrosion susceptibility. The higher susceptibility to corrosion of the 60% cold-worked and heat-treated sample can be attributed to the increase in the stored internal energy (induced residual stress resulting from the metastable processing) that was not completely removed by the subsequent heat-treatment process at 1,100°C for 1 h. In the current study, the cold-worked and heat-treated material produced the lowest polarization resistance (as shown in Tables 2 and 3), which indicates poor corrosion resistance and corresponding to the condition with qualitative significant reduction in the amount of δ -ferrite (Figure 3(b) & (c)) compared to that observed in as-received (Figure 3(a)) specimen.

It is evident from the data in Table 2 and polarization curves of the corresponding Stern Geary analysis presented in Figure 4 for the 1 M sulfuric acid (H_2SO_4) environment, that the corrosion potentials recorded for all the samples are quite comparable in value. The current plateau observed at high anodic overpotential (for all the samples) is indicative of strong passivation tendencies. This behavior can be associated with concentration polarization owing to the relative high content of Cr and Ni in the austenitic stainless steel.

3.4. Effect of heat treatment and cold working on corrosion susceptibility in NaCl

The results of the electrochemical test and polarization curves for specimen subjected in 1 M NaCl environment are presented in Table 3 and Figure 5. Although the severity of the corrosion is lower in NaCl compared to that obtained in the H_2SO_4 environment, the pattern of corrosion is comparable in the samples for media. The as-received stainless steel material has the lowest corrosion rate, while the 60% cold-worked plus heat-treated sample is the most susceptible to corrosion among the

Table 2. Corrosion rate and polarization resistance of specimens tested in an acidic environment

Sample condition	Corrosion rate (mm/yr)	Polarization resistance (Ω)	I_{corr} (A/cm ²)	Standard deviation σ_i	E_{corr} (V)	Standard deviation σ_v
As-received	0.95273	174.58	8.20×10^{-5}	0.00716117	-0.34233	0.14478
Heat treated	1.1127	150.54	9.58×10^{-5}	0.087288	-0.34031	0.144472
60% cold worked and heat treated	1.3081	138.19	1.13×10^{-4}	0.004921	-0.33197	0.144718

Figure 4. Potentiodynamic polarization curves of specimen tested in Acidic (H₂SO₄) environment.

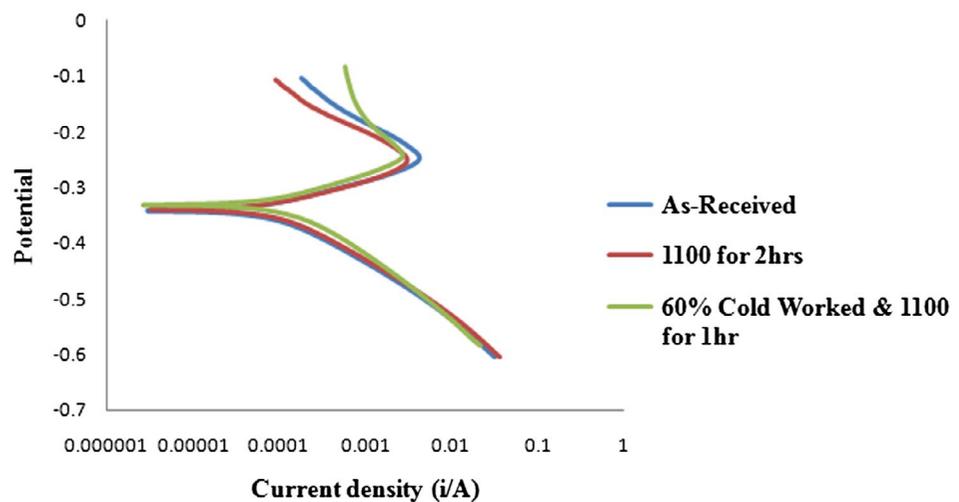
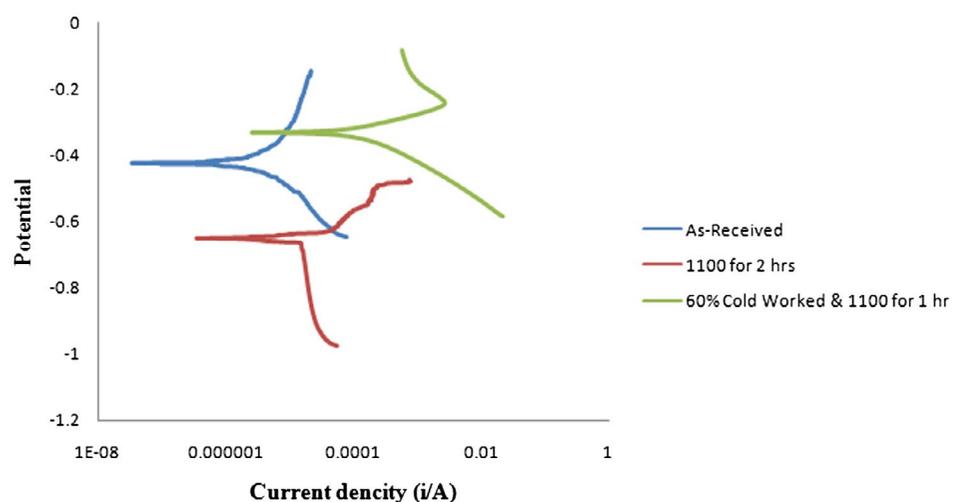


Table 3. Corrosion rate and polarization resistance of specimens tested in a basic environment

Sample condition	Corrosion rate (mm/yr)	Polarization resistance (Ω)	I_{corr} (A/cm ²)	Standard deviation σ_i	E_{corr} (V)	Standard deviation σ_v
As-received	0.009424	10,224	8.11×10^{-7}	0.000020288	-0.42161	0.144808
Heat treated	0.10056	1,457.1	8.65×10^{-6}	0.00013147	-0.40959	0.144689
60% cold worked and heat treated	0.57534	291.75	4.95×10^{-5}	0.004918	-0.33337	0.144718

samples in the NaCl environment. Overall, the presence of δ -ferrite in the as-received wrought stainless steel material does not damage its corrosion resistance in the acidic and basic environments. In contrast to the corrosion behavior of the samples tested in the acidic environment, there is significant difference in the corrosion potentials recorded for the samples in the NaCl environment. In particular, the polarization curves obtained for the samples tested in the NaCl environment showed that the samples are far more active (especially the heat-treated sample at 1,100°C) compared to the behavior of those tested in the acidic environment. This difference in corrosion behavior may be attributed to the microstructural modification (less δ -ferrite) resulting from the heat-treatment

Figure 5. Potentiodynamic polarization curves of specimen tested in Basic (NaCl) environment.



process. Also, the heat-treated sample at 1,100°C showed some perceptible pitting on the surface, which may be attributed to the localized damage of the passive film from environmental aggressiveness.

4. Conclusion

The results of the investigation on the influence of δ -ferrite on corrosion propensity of austenitic stainless steel in acidic and basic media showed that the formation of delta ferrite, known to involve the preferential segregation of chromium to form precipitate, has a similar pattern to the formation of $M_{23}C_6$ precipitate. However, the formation of δ -ferrite does not degrade and or inhibit the inherent resistance to corrosion of the austenitic stainless steel sample as generally reported with the $M_{23}C_6$ precipitates. Additionally, in acidic and basic environments, the 60% cold-worked plus heat-treated specimen, with reduced δ -ferrite content showed more susceptibility to corrosion than the as-received stainless steel sample with higher amount of δ -ferrite.

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