

Effect of Sensitization on The Corrosion of Austenitic Stainless Steel in Fresh Water

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Abstract: *In this research work, the Impact of Sensitization on the Corrosion of austenitic stainless steel, type 304 and 316 when immersed in fresh water was investigated in detail. A set of samples has been normalized by soaking the steel at a temperature range of 550°C – 750°C followed by air cooling. On the other hand, a total of five sets of the samples of steel were given sensitization treatment by holding at a temperature range of 550 – 750°C for different soaking time periods ranging from 30 minutes, 1 hour, 3 hours, 5 hours and 10 hours. The microstructure of the sensitized samples was observed under inverted metallurgical microscope. The corrosion rate of austenitic stainless steel type 304 and 316 was also determined using the total immersion technique. The corrosion medium was fresh water. The result derived from the corrosion immersion technique indicated that the corrosion rate for stainless steel type 304 increases progressively with increase in immersion time, while for stainless steel type 316 decreases progressively with increase in immersion time*

Keywords: *Sensitization, Austenitic Stainless Steel, Corrosion, Microstructure*

I. Introduction

Stainless steels have a very good corrosion resistance when properly heated and used in a low temperature environment. Sometimes, they are susceptible to corrosion when exposed to temperatures between 550°C – 750°C (1-4). This is because the formation of Cr-rich Carbides at the grain boundaries and neighboring matrix, leaving a Cr-depleted zone extending to both side of the grain boundaries.

The importance of austenitic stainless steel (ASS) in the petroleum industries cannot be over emphasized. Its excellent properties which range from high tensile strength, good impact, wear and corrosion resistances have found many applications in the petroleum industries. This material is use in almost all environments that need an optimization of these properties, some of which are, Fossil-fired power plant, flue gas desulphurization equipment. (5-7). ASS is known for its corrosion resistance principally due to the presence of chromium which is soluble in the austenitic matrix. Chromium adds to the overall corrosion resistance through a passivation process by forming a complex spinel-type [(Fe, Ni) O (Fe, cr)₂O₃] passive film (8-10).

Austenitic stainless steels (ASSs) have a dominant position in the group of SSs. Austenitic stainless Steels are the most favoured construction materials of various components required in the chemical, petrochemical and nuclear industries. The exposition in the temperature range of 550°C-750°C leads to the precipitation of M₂₃ C₆ chromium-rich Carbide on the grain boundary and to the formation of the chromium depletion regions. If the chromium content near the grain boundaries drop under the passivity limit 12 wt. %, the steel becomes to be sensitized (11-14).

Sensitization is a major problem in stainless steels that affects the alloy's durability. Chromium additions in steel is the main contributor to sensitization.

Sensitization is defined when a carbide precipitation induced by the welding process or heat treatment can cause chromium-depletion near the grain boundaries. Chromium is extremely reactive with oxygen and will form a very thin chromium oxide layer on the surface of stainless steel. Sensitization treatment significantly modifies the stress corrosion cracking behaviour and the cause of this is the intergranular precipitation and the grain boundary chromium depletion (15).

Corrosion studies of metallic structures remain a major area of interest for scientific investigation, Recent effort in the study of mild steel and AISI 304L stainless steel in the presence of dissolved ions in seawater was recently reported (16) in which the copper ions were found to have pronounced effect on corrosion rate.

II. Materials And Method

The materials used for this work include austenitic stainless steel 304 and 316 grade. This special grade of steel were sourced from NNPC Warri. The chemical composition is shown in table 1 at Turret Engineering service Ltd, Port Harcourt, Nigeria.

Five set of each coupon were given sensitization treatment under different soaking time of (30mm, 1 hour, 3 hours, 5 hours and 10 hours), in the temperature range of 50°C-750°C, using a digital heat treatment furnace, and cooled in air (normalized).

Five coupons each of both materials was full immersed in five beakers containing the corrosion medium with fresh water, labeled. The coupons were cleaned with soft brush and air dried in every two days intervals for weight loss reading for the total exposure time of 42days, a digital balance is used for the reading. The corrosion rate in each of the plastic beakers was calculated for various steel coupons. Another five coupon each of both materials in the treated condition was cut before the corrosion test, to serve as a control specimen for metallographic studies. The coupons were mounted and ground progressively on emery grit papers (220-1000 grits) with water as the coolant. The ground coupon was then polished with diamond polishing paste, and etched with freshly prepared oxalic acid (HCL) and distilled water in the ratio 30:70. The micrograph of each etched coupons were viewed under a metallurgical microscope using a magnification of X 100.

Table 1. Chemical Composition of Austenitic Stainless Steel Type 304 and 316

| TYPES | Fe(%) | Mn(%) | Cu(%) | V(%) | Co(%) | Cr(%) | Ni(%) | Mo(%) | Ti(%) |
|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|
| 304 | 69.40 | 1.25 | 0.22 | 0.07 | - | 18.82 | 9.99 | 0.26 | - |
| 316 | 67.48 | 1.48 | 0.17 | 0.06 | 0.27 | 17.61 | 11.00 | 1.92 | 0.09 |

III. Results And Discussion

The corrosion rate was computed in mils per year (mms) with the standard expression (17-19).

$$C.R = 3.45 \times 10^6 W$$

$$\rho \times A \times T$$

Where W is weight loss in mg. ρ is the density of the coupons in g/cm^3 , A is the exposed area in square cm^2 , and T is the exposure time in hours (17).

Fig. 1 show the plots of weight loss of ASS 304 and 316 vs time after immersion in fresh water for 1008 hours. However, it is observed that the weight loss in ASS 304 increased progressive whereas the opposite effect is been observed for ASS 316 as it's progressively decreased. This response can be attributed to increases in the time of exposure for the sensitization of ASS 304 and 316 coupons. From the chemical composition of ASS 304 (Table1), Molybdenum is in trace. Which could have enhanced corrosion resistance is conspicuously low in the matrix of ASS 304. Fig. 2 shows the comparative plots of the corrosion rates of ASS 304 and 316 vs immersion time. A decrease in corrosion rate of ASS 316 with increasing immersion time was also observed following similar method when compared to the weight loss whereas the opposite effect was observed for ASS 304 as its progressively increases.

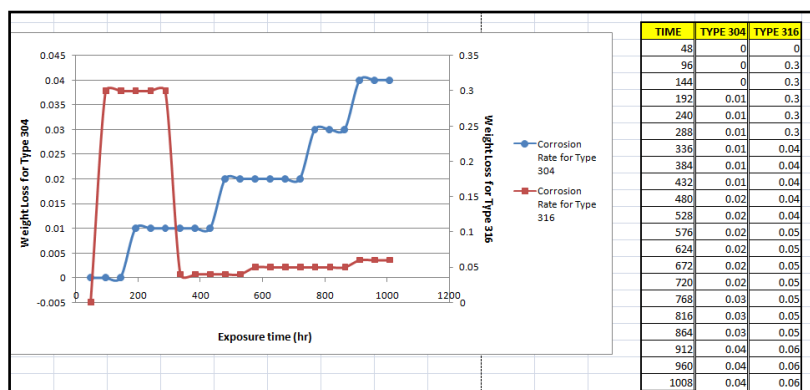


Fig. 1. Weight loss of ASS 304 and 316 in fresh water

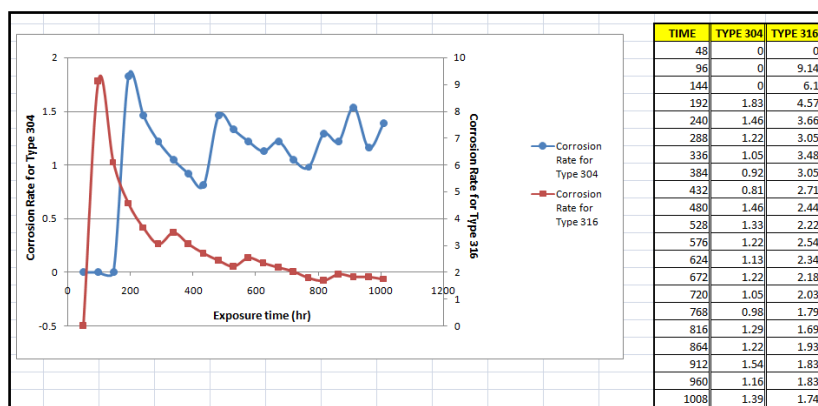


Fig. 2. Corrosion rate of ASS 304 and 316 in fresh water

Fig. 3 shows the microstructure of ASS 304 before and after sensitization time for the soaking time interval of 30min, 1hours, 5hours and 10hours at the temperature range of 550°c-750°c, depicting the chromium depleted morphologies of the experiment.

The microstructures of ASS 304 showed that the chromium depleted zone progressively increases with increase in sensitization time. Fig. 4 shows the microstructures of ASS 316 before and after giving sensitization treatment for 30min, 1hours, 3 hours, 5 hours and 10 hours it shows the morphologies of the chromium depleted zone. The chromium depletion also increases progressively with increase in sensation time but not as of ASS 304



Before sensitization SS 304



SS 304 Sensitized for 30 min



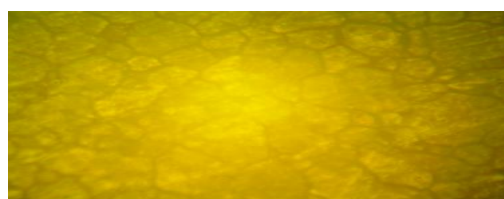
SS 304 Sensitized for 1 hours



SS 304 Sensitized for 3 hours



SS 304 Sensitized for 5 hours



SS 304 Sensitized for 10 hours

Fig. 3. Microstructure of ASS 304 before and after sensitization at 550°c – 750°c



Before sensitization SS 316



SS 316 Sensitized for 30 min



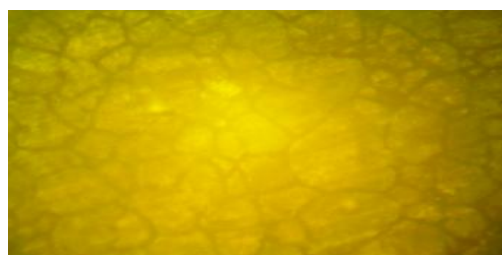
SS 316 Sensitized for 1hours



SS 316 Sensitized for 3 hours



SS 316 Sensitized for 5 hours



SS 316 Sensitized for 10 hours

Fig. 4. Microstructure of ASS 316 before and after sensitization at $550^{\circ}\text{C} - 750^{\circ}$

IV. Conclusion

From the obtained results and analysis related to the corrosion behavior of austenitic stainless steel type 304 and 316, with its associated metallography, the following conclusions are drawn.

- (1) The microstructure of Sensitized austenitic stainless steel type 304 and 316 showed an increase in the chromium depleted zone with increase in Sensitization time.
- (2) The corrosion rate of ASS type 304 increases progressively with increase in immersion time, while ASS type 316 decreases progressively with increase in immersion time.

References

- [1] R. Singh, J. Mater. Proc. *Techol.* 2006 (2008) 286
- [2] R. Singh, B. Ravikumar, A. Kumar, P.K. Dey, I. Chathova, *Metall. Mater. Trans. A* 34 (2003) 2441
- [3] G. Radenkovic, S.K. Zecevic, Z. Cvijovic, D. M. Drazic, *J.Serb. Chem. Soc.* 60 (1995) 53
- [4] H. Ma, S. Chem, C. Yang, J. Luo, *J. Serb. Chem. Soc.* 67 (2002) 435.
- [5] A Galal, N.F. Atta and M.H .S. Al-Hassan. *Effect of some ThioreDerivutives on the Electrochemical Behaviour of AISI 316 Austenitic Stainless Steel in Acidic Solutions Containing Chloride Ions: I. Molecular Structure and Inhibition Efficiency Relationship. Materials Chemistry and Physics* Vol. 89, No. 1, 2005, PP.38-48
- [6] A. I. Munoz, J.G. Anton, S.L. Nuevalos, J.L. Guinon and V.P. Herranz, "Corrosion Studies of Austenitic and Duplex Stainless Steels in Aqueous Lithium Bromide Solution at Different Temperatures," *Corrosion Science*, Vol 46, No. 12, 2004, pp. 2955-2978.
- [7] M.A. Stretcher, "Stainless Steels: Past, Present and Future," *Climax Molybdenum Co., Ann Arbor*, 1997.
- [8] T. Nakayama and Y. Oshida, "Identification of the Initial Oxide Films on 18-8 Stainless Steel in High Temperature Water," *Corrosion*, Vol. 21, 1968, pp. 336-337.
- [9] G. Okamoto and T. Shibata, "Passivity and Break down of Passivity of Stainless Steel," In: R.P. Frankenthal and J. Kruger, Eds., *Passivity of Metals Electrochemical Society, New York*, 1978.
- [10] J.A. Platt, A. Guzman, A. Zuccari, D.W. Thornburg, B.F. Rhodes, Y. Ossida and B.K. Moore, "Corrosion Behavior of 2205 Duplex Stainless Steel," *American Journal of Orthodontics and Denton Facial Orthopedics*, Vol. 112, 1997, pp. 69-79.
- [11] LO, K.K., SHEK, C.H., LAI, J.K.L. 2009. *Recent development in stainless steels. Materials science and Engineering: R: Reports*, 65, pp. 39-104.
- [12] PARVATHAVARTININ, DAYAL R.K. 2002. *Influence of Chemical Composition, Prior deformation and prolong thermal aging on Sensitization Characteristics of austenitic stainless steels. Journal of Nuclear Materials*, Vol. 305, pp. 209-219.
- [13] TRILLOT. A., MURR L.E. 1999. *Effects of Carbon Content, deformation and Interfacial Energetics on carbide Precipitation and corrosion sanitation in 304 stainless steel. Acta materialia*, vol.47 No. 1, pp.235-245.
- [14] TAVARES, S.S.M., MOURA, V., DACOSTA, V.C., FERREIRA, M.L.R., PARDAL, J.M. 2009. *Micriostuctural change and corrosion resistance of 3105 steel exposed to 600-8000c. material characterization*, 60, pp. 573-578.
- [15] MOHAMAD KHAIRUAZLAN BIN KAMARUZAMAN. "Investigation of chloride stress corrosion cracking in austenitic stainless steel." 2013.
- [16] M. Mobbin and H.shabnam, "corrosion behavior of mild steel and SS 304L in presence of dissolved copper," *journal of mineral's and materials characterization and engineering*, vol.9, No.12, 2010, PP, 1113-1130.
- [17] A.Y Badmos, H.A Ajimotakan and E.O. Emmanuel, "Corrosion in petroleum pipelines" *New York science journal*, Vol.2, No. 5, 2009, PP.36-40.
- [18] S.A, U.M. Eduok and E.E. Oguzie, "corrosion inhibition of mild steel in IM H2So4 by polyvinyl pyrrolidone and synergistic iodide Additives," *portugaliac Electrochemical Acta*, Vol.26, 2008, PP.533-546.
- [19] N.DPrasanna M.K.Muralidhara, M.K.Agarwal and K.Radhakrishna, "Mechanical Properties and Corrosion Characteristic of IS400/12 Grade Ductile Iron," *Transactions of 57th International Foundry Men Congress, Osaka*, / December 2009, PP. 89-95.