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Corrosion Rate of Stainless Steel 304 in HNO₃ Solution

Hendrikus Dwijayanto Wibowo Sutarjo^{1*}

¹ Department of Mechanical Engineering, Faculty of Science and Technology, Universitas Sanata Dharma, Yogyakarta, Indonesia

ARTICLE INFO

Keywords:

Corrosion rate
Mechanical engineering
Sulfuric acid
Stainless steel
Temperature

Corresponding author:

Hendrikus Dwijayanto Wibowo Sutarjo

E-mail address:

hdw_sutarjo@gmail.com

The author has reviewed and approved the final version of the manuscript.

<https://doi.org/10.37275/arkus.v7i1.90>

ABSTRACT

This literature review aims to describe corrosion rate stainless steel 304 in sulfuric acid. Immerse process do in 700C temperature for 6 hours and than in 290C temperature for 18 hours every day. This condition aim to get closer to the actual use in the manufacture of tubes of reactor SAMOP (sub critical assembly for Mo99Prad action). Specimen after TIG welding and electric arc welding cleaned from crust and than measured, drawing, balanced, and record the first weight. The survey findings show heavy shrinkage sample, it is well visible on the corrosion pH 0.5 in electric arc welding of 0.105 gram/dm²/month for corrosion 0.026 gram/dm²/month without welding and pH 0.2, arc welding of 0.045 gram/dm²/month, pH 0.2 no Las 0.02 gram/dm²/month. Specimen that has been welded have significant differences in corrosion rate compare to specimen that have not weld.

1. Introduction

The development of time and technology affects the diversity of human needs. The application of technology in industrialized countries is progressing rapidly. Almost all industrial equipment and machines and their components are designed so that maximum strength and service life can be known. This requires research time and high accuracy. A series of chemical processes are required to obtain steel with the desired mechanical properties, such as ductility, toughness, hardness, and corrosion resistance. In this literature review, the author explains the effect of HNO₃ solution with a pH of 0.2 and 0.5 on the corrosion rate of Stainless Steel 304. This type of stainless steel is used for the SAMOP

(Sub Critical Assembly for Prad Action) reactor tube. Furthermore, the parameters of temperature, time, and acidity are all made to resemble the actual operating conditions of the SAMOP reactor.

Stainless steel classification

With the rapid development of technology, nuclear benefits, formerly used as weapons of war, are now widely used to meet human needs. The utilization of nuclear technology has many advantages because of the nature of radiation that is easily detected to deficient levels, has excellent penetrating power, and can be controlled both in direction, beam area, and particle energy. Stainless steel is very suitable for the



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manufacture of test tubes for nuclear reactions. Using stainless steel is the SAMOP (Sub Critical Assembly for Prad Action) reactor tube.¹

Stainless steel

Stainless steel is an alloy of iron (Fe) with a minimum Cr content of 12%. The oxidation reaction between oxygen (O₂) and chromium (Cr) forms a protective layer (anti-corrosion protective layer). To improve the properties of stainless steel according to its application, other elements are also added. Other elements added include Ni (nickel), Mo (molybdenum), Co (copper), Ti (titanium), which function to increase resistance to temperature and corrosion. The main classes of stainless steel are austenite, ferrite, martensite, duplex.²

Austenite stainless steel

The austenitic composition of stainless steel is between 18% Cr and 8% Ni or commonly referred to as eighteen-eight stainless steel. Austenitic stainless steels have better rust resistance, formability, and weldability. This type is often used in various chemical industries for construction materials, kitchen furniture, turbines, jet engines, automobiles, rotating components, shipbuilding, and atomic reactors.³

Ferritic stainless steel

The chromium content is about 16% to 18%, and the nickel content is about 2%. Corrosion resistance is not very good and relatively difficult to fabricate or machine. An advantageous property of ferrite stainless steels is that it is difficult for stress corrosion cracking to occur without Ni content.⁴

Martensite stainless steel

The composition of martensitic stainless steel is 12%-13% Cr, and 0.1%-0.3% C. Cr content between 12%-13% is the lowest limit for acid resistance. Martensitic stainless steel has good heat resistance;

hardening and tempering can obtain good mechanical properties. This type of stainless steel is used for cutting tools and tools.⁵

Duplex stainless steel

Duplex stainless steel has two phases, namely austenite and ferrite phases. Generally, it has a composition of 12% Cr + 5% Ni + 1.5% Mo + 0.03% C. It has a combination of austenite and ferrite properties that cover each other. For example, the low creep stress of austenite properties is improved in the presence of ferrite properties. Moreover, the low ductility of ferrite properties is improved by the properties of austenite. Corrosion resistance generally exceeds 18-8 steel, especially steel, which has a high Cr content and contains Mo, which is very good in pitting corrosion resistance. This steel can be used for heat exchangers using seawater.

The effect of alloy elements on stainless steel

In application, stainless steel is not only needed as a metal that is resistant to corrosion but additional properties are also needed to improve its mechanical properties. This increase in mechanical properties depends on the number of elements contained in stainless steel. Additional elements in stainless steel include the following; Chromium (Cr) is valid for forming a passive layer to protect against corrosion. Nickel (Ni), as an austenite stabilizer, improves mechanical properties and increases corrosion resistance in acidic mineral environments. Manganese (Mn) helps the function of Ni. Molybdenum (Mo) is a passive layer stabilizer in an environment that contains a lot of chloride ions (Cl⁻), such as seawater (NaCl). Carbon (C) increases the hardenability of stainless steel materials. Nitrogen (N) forms duplex stainless steel by increasing the formation of austenite, improving the mechanical properties of Stainless Steel.



Metal corrosion

Stainless steel (SS) is not a precious metal like gold (Au) & platinum (Pt) which almost does not corrode due to the influence of environmental conditions, while SS still corrodes. The corrosion resistance of SS is due to the presence of an invisible layer that occurs due to the oxidation of SS with oxygen which eventually forms a protective anti-corrosion layer. The source of oxygen can come from air or water. Other materials with similar properties include titanium (Ti) and aluminum (Al). In general, the protective layer is formed from the reaction of chromium + oxygen spontaneously to form chromium-oxide. If the S oxide layer is scratched/peeled off, the protective layer will immediately form spontaneously, of course, if the environmental conditions contain sufficient oxygen. However, environmental conditions still cause damage to the protective layer. In situations where the protective layer can no longer be formed, corrosion will occur. Many media can cause corrosion, such as air, acidic/alkaline liquids/solutions, process gases (e.g., flue gases from combustion chamber exhaust or other chemical reactions), metals of different types, and interconnected.^{3,5}

Types of corrosion in stainless steel

Although the main reason for using stainless steel is its corrosion resistance, the selection of suitable stainless steel must also be matched to the proper application. In general, corrosion causes several problems such as the formation of small/fine holes in tanks and pipes causing liquid or gas leakage, decreased strength of the material due to shrinkage or reduction in thickness or volume of the material so that the strength also decreases, resulting in cracks, bending, broken. The surface of the material becomes unattractive due to rust crust or holes and the formation of rust that may contaminate other substances or materials. This is highly avoided,

especially in the food production process. In general, corrosion of stainless steel can be categorized as follows: uniform corrosion, pitting corrosion, crevice corrosion, stress corrosion cracking, intergranular corrosion, and galvanic corrosion.^{1,3}

Uniform corrosion

Uniform corrosion occurs due to partial or complete damage to the protective layer on the SS so that the SS will be evenly reduced. This corrosion occurs generally caused by hot liquids or solutions of strong acids or alkalis. Hydrochloric acid and hydrofluoric acid are environments that need to be avoided by SS, especially when combined with high temperatures and concentrations.

Pitting corrosion

Corrosion in the form of small holes the size of a needle starts from local corrosion (not like uniform corrosion). This pitting corrosion initially looks small on the surface of the SS but gets more prominent on the inside. This corrosion occurs in several conditions in an environment with a low pH, moderate temperature, and a reasonably high chloride concentration (e.g., NaCl or salt in seawater). At a sufficiently high chloride concentration, initially, chloride ions damage the protective layer on the SS surface, especially the defective surface. The appearance of these defects can be caused by sulfide impurities, small cracks due to grinding, welding, scale buildup, solid solution buildup.

Generally, SS with high chromium (Cr), molybdenum (Mo), and nitrogen (N) content tends to be more resistant to pitting corrosion. In the petrochemical industry, this corrosion is very dangerous because it attacks the surface and the visual appearance is very small, making it difficult to overcome and prevent, especially in high-pressure pipes. The material's resistance to pitting corrosion of this type is formulated as follows.

$$\text{PREN} = \% \text{Cr} + (3,3 \times \% \text{Mo}) + (16 \times \% \text{N})$$



One thing that causes pitting corrosion is severe that when a small hole is formed, this hole will continue to grow (bigger and deep) even though the SS condition is very closed or cannot be touched at all. Therefore, in designing materials for a work environment where pitting corrosion is likely to occur, the PREN value is used as a reference. For example, when comparing austenitic SS such as 304, 316L, and super-austenitic SS such as UR 6B. SS 304 has the composition (in %): < 0.015 C, 18.5 Cr, 12 Ni while for SS 316L has the composition: < 0.030 C, 17.5 Cr, 13.5 Ni, 2.6 Mo. The super-austenitic SS UR 6B has the following compositions: < 0.020 C, 20 Cr, 25 Ni, 4.3 Mo, and 0.13 N. With different compositions, the PREN values for each SS are: 304 = 18, 316L = 26, and UR B6 = 37. Thus, UR B6 has the strongest pitting corrosion resistance while 304 has the weakest pitting corrosion resistance.

Crevice corrosion

This type of corrosion often occurs in areas where the oxidation state of chromium (Cr) SS is very low or even non-existent (poor oxygen). It often also occurs due to the design of equipment construction that does not allow oxidation, for example, gaps between gaskets/packing, gaps formed due to imperfect welding, narrow corners, gaps/corners between 2 or more metal layers, and gaps between nuts/bolts. Crevice corrosion can be viewed as pitting corrosion which is more severe and occurs at temperatures below the moderate temperatures that usually cause pitting corrosion. One way to avoid this problem is to make the design of the equipment more 'open' even though, in reality, it is challenging for all applications.

Stress corrosion cracking

Under conditions of a combination of stress (both tensile, torsion, compressive and thermal) and a corrosive environment, SS tends to corrode faster. Rust, which reduces the SS surface's effective cross-

sectional area, causes the working stress on the SS to increase. This corrosion can also occur, for example, on pins, bolts with holes/mounts, SS, which has residual stress due to rolling, bending, and welding.

This corrosion increases if the stressed part is in a high chloride content environment, such as seawater, where the temperature is relatively high. As a result, the application of SS is limited to handling hot liquids at temperatures above 50 0C even with shallow chloride levels (a few ppm). SS suitable for this corrosion is austenitic SS due to its relatively high nickel (Ni) content. Grade 316 is not significantly more resistant than 304. Duplex SS (e.g., 2205/UR 45N) is more resistant than 304 or 316, even up to 150oC application temperature, and super duplex will be even more resistant to stress corrosion cracking. In some cases, this corrosion can be reduced by shelling the metal surface with metal sand grains or annealing after the SS is finished machining to reduce the stress on the metal surface.

Intergranular corrosion

Imperfections of the SS microstructure cause this corrosion. When austenitic SS is at a temperature of 425-850o C (sensitizing temperature) or when heated and allowed to cool slowly (such as after welding or cooling after annealing), the carbon will attract chromium to form chromium carbide particles in the grain boundary region. (grain boundary) SS structure. The formation of chromium carbide, which is concentrated at the grain boundaries, will eliminate/reduce the protective properties of chromium in the center of the grain. So this area will be easily attacked by corrosion. Generally, SS with a carbon content of less than 2% is relatively resistant to this corrosion. These microstructural imperfections are corrected by adding elements with a greater carbon affinity to form carbides, such as Titanium (e.g., in SS 321) and Niobium (e.g., in SS 347). Another way is to use low carbon grade SS



marked index 'L' -low carbon steel- (e.g., 316L or 304L). SS with a high carbon content will resist this type of corrosion as long as it is used at high temperatures (e.g., 304H, 316H, 321H, 347H).

Galvanic corrosion

Galvanic corrosion occurs due to the different connections of the material (2 different materials are electrically connected/connected, for example, bolts with nuts, rivets/rivets with the tank body, the result of welding with the workpiece) and/or immersed in an electrolyte solution, so that the dissimilar material becomes a kind of connection electricity. This mechanism is caused by one material functioning as an anode and the other as a cathode so that an electrochemical bridge is formed. With the occurrence of this electrical connection, the anode metal will be more easily corroded. The sequence is shown in the following metal electrochemical series. The metal on the left tends to be the anode (easy to rust), while the metal on the right tends to be the cathode. This galvanic corrosion depends on the difference in dissimilar material glory and the dissimilar material surface area ratio.²

Tungsten shielded welding (TIG)

This process is a welding method in which an electric arc is maintained between a non-consumable, substantially independent tungsten electrode, in an atmosphere of pure argon, with or without minor amounts of other beneficial gases. The gas shield prevents contamination of the weld metal by air. The surface of the aluminum alloy is covered by a layer of high melting point refractory oxide, which must be removed before a satisfactory weld can be made. A filler wire may also be added to the front edge of the pool of liquid to form a weld. It is one of the properties of the alternating current arc that it removes substantial oxides during the welding process. The TIG welding process is used when neat, high-quality, and economical welds are required for

thicknesses up to 6 mm. For thicknesses greater than 6 mm, MIG welding or other metal arc welding processes are usually used. Root holes in pipe joints with or without fusible inserts are penetrated using TIG welding as penetration can be controlled to provide a smooth flush finish.

Electric arc welding

Electric arc welding is one way to connect metal by using an electric arc that is directed at the metal surface to be joined. In part, affected by the electric arc, it will melt, as well as the electrode that produces the electric arc will melt at the end and propagate until it runs out. The molten metal from the electrode and part of the object to be joined is mixed and fills the gap between the two metals to be joined, then solidifies, and the two metals are connected. Electric arc welding machine can deliver a large enough electric current but with a safe voltage (less than 45 volts). The electric arc that occurs will generate high enough heat energy to melt the affected metal easily. The amount of electric current can be adjusted according to the needs by paying attention to the size and type of the electrode. In arc welding, the connection is made by the heat generated by the electric arc that occurs between the workpiece and the electrode. The electrode or filler metal is heated until it melts and is deposited on the joint so that a welded joint occurs. At first, there is contact between the electrode and the workpiece so that current flows, then by separating the conductors, an arc arises. Electrical energy is converted into heat energy in an arc, and the temperature can reach 5500 °C. There are three types of metal electrodes, namely plain electrodes, flux electrodes, and thick-coated electrodes. Plain electrodes have limited use, including for wrought iron and mild steel. Usually, direct polarity is used. Welding quality can be improved by applying a thin layer of flux to the welding wire. The flux helps dissolve and prevents the formation of unwanted oxides. However, the coated



welding wire is the type most widely used in various commercial welding.^{1,3}

2. Conclusion

There is a significant difference in the rate of corrosion in the HNO₃ solution between the test object that has undergone welding and the test object that has not undergone welding. All of them were equally corroded either by welding or not, but the highest corrosion was found in electric arc welding. Corrosion occurs evenly on the entire surface of the test object due to partial damage to the protective layer. The highest corrosion rate at pH 0.5 is 0.245 gram/dm²/week, while the highest corrosion rate at pH 0.2 is 0.223 gram/dm²/week.

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