Corrosion Behavior of Austenitic Stainless Steel in Sulphuric Acid at Various Concentrations

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ABSTRACT

The susceptibility and resistance of type 304 austenitic stainless steel exposed to sulphuric acids (0.3M to 1M concentrations) at ambient temperatures and at higher temperatures were investigated. Weight loss method was used to examine the corrosion rate of the steel after immersion in the corrosive media. The Constant Extension Rate Tensile Test (CERT) was also performed with a tensometer to determine the susceptibility of the steel to stress corrosion cracking in the corrosive media. This paper reports the observed susceptibility of type 304 austenitic stainless steel to stress corrosion cracking in the corrosive media and its high resistance to uniform corrosion of below 0.1mm/yr.

Keywords: SCC, Sulphuric Acid, Austenitic Stainless Steel

INTRODUCTION

Corrosion is the destruction of a material resulting from exposure and interaction with the environment [1]. Corrosion remains one of the most severe limitations for the use of various steels in the chemical and petrochemical industries. Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel [2].

Despite the introduction of polymers and composites in recent years, metals remain important in structures because of their strength, stiffness, toughness and tolerance of high temperatures. The noble metals, such as gold and platinum are an exception to this, but they are rather too rare for common use [3].

Although one of the main reasons why stainless steels are used is corrosion resistance, they do in fact suffer from certain types of corrosion in some environments and care must be taken to select a grade which will be suitable for the application [2]. Corrosion can cause variety of problems, depending on the applications and the environment.

Corrosion occurs in many forms in structures made of these steels during service in various media. Some of these forms are intergranular [4, 5] pitting, sulphide stress cracking, chloride stress cracking [6, 7] and stress corrosion cracking [8, 9, 10]. Weld decay is also common in sensitized stainless steel structures [11, 12]. The consequences of these forms of corrosion are obvious; varying from enormous material losses to unreliability of operating the equipment which may lead to catastrophic consequences involving both men and money [13].

High corrosion resistance of austenitic stainless steels is primarily attributed to the passive oxide film formed on its surface, exposed to an aqueous solution, which is a mixture of iron and chromium oxides, with hydroxide and water-
containing compounds located in the outermost region of the film, and chromium oxide enrichment at the metal-film interface [14]. However, the resistance of this passive film is determined by the environmental conditions which the stainless steel is exposed to, as well as the alloy composition.

Tetraoxosulphate (VI) acid (Sulphuric) is the corrosive media used in this work. It is produced more than any other chemical in the world. It has large scale uses covering nearly all industries, such as fertilizer industries, petroleum refinery, paint industry, steel pickling, extraction of non-metals, and manufacture of explosives [15]. In chemical industries, it is used for the production of dyes, pharmaceuticals and fluorine.

In this work, the acid used is further used at higher temperatures above room temperatures to enhance breakdown of passivity. The present investigation aims at evaluating the corrosion resistance of type 304 austenitic stainless steel at different concentrations of tetraoxosulphate (VI) acid and at various temperatures to determine its viability and usefulness. It is hoped that the results from this investigation will make a further contribution to the existing knowledge in the selection of type 304 stainless steel for further industrial and environmental use.

MATERIALS AND METHODS

Material
The material used in this study is a 5mm diameter type 304 austenitic stainless steel. The chemical composition and mechanical properties as supplied by the manufacturer are shown in Table 1. The tensile specimen were prepared from this material using the lathe machine as shown in Figure 1. They were machined from round bars to the required specifications. They were then washed and degreased with acetone. The entire procedure was carried out according to (ASTM, 1989/1990).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>S</th>
<th>Ni</th>
<th>Si</th>
<th>Mo</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.06</td>
<td>0.005</td>
<td>8.03</td>
<td>0.45</td>
<td>0.03</td>
<td>1.40</td>
<td>18.95</td>
<td>Bal</td>
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Figure 1 Tensile test specimen

Experimental procedure
All the specimen were immersed at the same time in the experimental media which was sulphuric acid at concentrations of 0.3M, 0.5M, 0.7M, 1M. A specimen was removed from each of these acids after every seven days and the constant extension rate tensile test (CERT) was performed with a tensometer at a strain rate of 0.003cm/sec according to the method of Yawas[18]. As straining continued, the load extension curves were plotted by intermittently depressing the pin against the rotating drum which bore the graph paper on the tensometer. This operation continued until the specimen fractured. Percentage reduction in area of each test piece was recorded. This test was carried out according to the methods of Le and Ghali[16], Rondelli et al [17] and Yawas[18].

Corrosion test at various temperatures
Previously weighed coupons were suspended in each of the experimental media at an ambient temperature of (30°C). The first and second sets of coupon were retrieved from their corrodants after 7 days and 14 days intervals and the subsequent sets were retrieved after 21 days, 28 days and 35 days. They were then chemically cleaned in 20% sodium hydroxide containing 200g/L of zinc dust in order to remove the corrosion product. After rinsing in distilled water and absolute ethanol, the coupons were dried and weighed and the reading taken to the nearest 0.0001g on a mettle AE166(Delta range) analytical balance according to the method of Chen et al [19], Ashassi-Sorkhabi et al [20] and Jabeera et al [21].
In order to study the effect of temperature the above weight loss test was carried out in all the experimental media at higher temperatures of 40°C, 50°C, 60°C, 70°C, and 80°C using a thermostat water bath. Each specimen was retrieved after and interval of 4 hours. The difference in weight of the specimen was again taken according to the method of Yawas[18].

RESULTS

The results are shown in figures 2 to 8.

![Figure 2. Variation of % Elongation to fracture against time for steel immersed in 1M H2SO4](image)

![Figure 3. Variation of % Elongation to fracture against concentration for steel immersed in H2SO4 after exposure for 7 days](image)
Figure 4. Variation of % Reduction in cross sectional area against time for steel immersed in 1M H$_2$SO$_4$

Figure 5. Variation of % Reduction in cross sectional area against concentration for steel immersed in H$_2$SO$_4$ after exposure for 7 days

Figure 6. Variation of corrosion rate against exposure time for steel immersed in 1M H$_2$SO$_4$
Figure 7. Variation of corrosion rate against concentration for steel immersed in H$_2$SO$_4$ after exposure for 7 days.

Figure 8. Variation of corrosion rate against temperature for steel immersed in H$_2$SO$_4$ after exposure for 4 hours at 1M concentration.

DISCUSSION

Stress corrosion cracking of the steel.

Figures 2, 3, 4 and 5 show the SCC behaviour of type 304 austenitic stainless steel in dilute H$_2$SO$_4$ and expressed in terms of percentage elongation to fracture and in terms of reduction in cross sectional area. These parameters were derived following the procedures of McIntyre and Dillion[22], Beaver and Koch[23]. From the figures it can be observed that both the percentage elongation and reduction in cross sectional area decreased with increased exposure time and increased concentration. Owing to the low nickel and molybdenum contents austenitic stainless steel type 304 is susceptible to stress corrosion cracking in environments rich in hydrogen sulphide.

Uniform Corrosion of the steel

In figure 6 above a decrease in corrosion rate as exposure time increases was observed. This is because there remains no direct contact between metal surface and corrosive ions by corrosion products and excess of cations near the metal surface as reaction proceeds which is in consonance with findings of Dillion[24].

Figure 7 shows an increase in corrosion rate as concentration increases.
The results also show a corrosion rate of below 0.1 mm/year at ambient temperature. This indicates high resistance to corrosion in these environments at ambient temperature. The high chromium content which forms chromium oxide passivation on the surface of steel protects it from further corrosion. The 8.03% nickel contained in the steel assists in providing resistance to uniform corrosion in moderately reducing environments of H$_2$SO$_4$ at low concentrations.

**Effect of temperature on corrosion of steel**

Figure 8 shows an increase in corrosion rate as temperature increases. At a constant time of four hours and at temperatures of 40$^\circ$, 50$^\circ$, 60$^\circ$, 70$^\circ$, 80$^\circ$C, it was also observed that there was no significant weight loss in steel, probably due to the short time of exposure. When compared to weight loss at room temperature of about 30$^\circ$C after a period of 21 days it shows the length of time of exposure also plays an important role in the corrosion of the steel as established by Yawas[18].

**CONCLUSION**

The following conclusions can be drawn on the study undertaken on corrosion behaviour of type 304 austenitic stainless steel in H$_2$SO$_4$.

i. The ductility of Type 304 Austenitic stainless steel decreased with increased exposure time and concentration, an indication that it is susceptible to stress corrosion cracking in dilute H$_2$SO$_4$.

ii. The corrosion rate decreased with increase in exposure time.

iii. The corrosion rate of the steel increased with increase in temperature.

iv. Though the steel was highly resistant to uniform corrosion in these environments it was still found to be susceptible to SCC.

v. Hydrogen sulfide are principal agents in environments causing stress corrosion cracking e.g sea water, oil and gas industries.

vi. The mechanism of SCC involves the conjoint action of the environment and the presence of a tensile stress.

**REFERENCES**


