Role of heat tint on pitting corrosion of 304 austenitic stainless steel in chloride environment

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Abstract

The effect of simulated heat tint produced by air oxidation at a wide range of temperatures 200, 400, 600, 800 and 1050 ºC on pitting potential of 304 austenitic stainless steel was studied in environment of different chloride concentration. It was found that the heat tint effect depends on the heating temperature.

The most effective heat tint was that produced at the high temperature up to 1050 ºC and hence less pitting potential and low corrosion resistance. In order to improve the surface pitting corrosion resistance, acid pickling of hydrochloric acid was applied at different time and temperatures of 15 & 60min, room temperature and 60 ºC respectively. Improvement in pitting potential was achieved as the pickling time and temperature increase. This is can be attributed to the removal of depleted chromium oxide film produced during the heat tint.

Keywords: stainless steel, heat tint, pitting potential, acid pickling

Introduction

Stainless steels are chosen for various service because of primary good corrosion resistance and good mechanical properties and in addition of their appearance and for their freedom from contamination of production in storage and shipment. Susceptibility of stainless steels to corrosion process can be markedly influenced by the presence of the oxide film, which strongly modified the surface properties of the alloy. [1]

Regions of the oxide film that are susceptible to breakdown can act as pitting initiation sites. The condition created by welding, brazing, annealing and stress relieving operations can produce a surface oxide film and reduce localized corrosion resistance. [2] Welding of stainless steels alloys can produce oxide scale or heat tint composed of elements that have been selectively oxidized from the base metal, principally iron and chromium. The defects and stress within the heat tint oxide layer make it a poor barrier to any corrosive media. In chromium depleted layer of base metal beneath the heat tint is significantly less resistant to localized corrosion than the base metal in certain environments, such as chlorides.

Experimental

-Material
The work was carried out on annealed and air oxidized at (200, 400, 600, 800 and 1050°C) 304 austenitic stainless steel samples. The chemical composition for the used samples was same as following: 18%Cr, 8%Ni, 0.08%C, 1%Si, 2%Mn, 0.045%P, 0.03%S.

In order to obtain flat and surface free from both mechanical disturbance and chemical residual a rough grinding from 200 grit paper to diamond paste polishing were carried out. This mechanical cleaning was followed by chemical cleaning using distilled water and acetone washing and drying using hot air.

Air oxidation to produce simulated heat tint scale surface was carried out at open furnace at the determined range of temperatures for 30 minutes followed by air cooling. These samples were exposed to pitting corrosion tests with the same scale produced by air oxidation where the same number of samples was tested after acid pickling (5%HF & 15%HNO₃ & 80%H₂O) at room and 60°C temperatures. This acid pickling aimed to remove the surface scale (heat tint).

-Corrosion tests

Electrochemical studies of the samples with and without heat tint were carried out. Pitting potential was determined for each samples after potentiodynamic scan at 10 mv/sec. Corrosion tests were performed using Bank potentiostat at media containing different chloride concentration of 200ppm, 500ppm, 1000ppm and 22000 ppm Cl⁻.

Experimental Results

-Effect of heat tint:

Heat tint produced on 304 stainless steel samples is shown in figure 1. The results of pitting potentials for as received and heated (heat tinted) samples tested in different chloride concentrations of (200ppm, 500ppm, 1000ppm and 22,000ppm) at room temperature are shown in figure 2. It is clear that the pitting potential decrease as the oxidation temperature and chloride concentration increase.

At 200°C, heat tint found to improve the pitting potential where the pitting potential found to be slightly higher than that observed for as-received samples. In contrast, the heat tint produced at temperatures of 400, 600 and 800°C had drastic effect on the pitting potential, where more active pitting potential and less corrosion resistance was obtained.

Figure1. Photograph shows heat tint produced on 304 austenitic stainless steel samples after oxidation at different temperatures.
Figure 2. Relationship between the pitting potential and heating temperature (oxidation temp.) for 304 stainless steel specimens tested in aqueous solution containing different concentration of chloride ions.

- Effect of acid pickling:

Pickling usually means removing the relatively heavy, dark oxide films caused by annealing or high temperature thermal stress relief conducted in oxidizing atmosphere.[1] In this work Pickling had achieved good improvement in corrosion resistance (pitting potential). This was observed when both pickling were carried out at room temperature as well as at 60°C as shown in figures 3 & 4.

- Pickling at room temperature

Figure 3, shows the pitting potential for samples after acid pickling at RT for 200min. It’s clear that the acid pickling has good improvement in pitting potential. Pickling process improves the pitting potential where less active potential was achieved.
The other observation when the heating was increased above 200ºC, less improvement in pitting potential was observed. In another word the improvement in pitting potential was found to depend on the heat tint temperature and the chloride concentration.

![Graph](image)

**Figure 3.** Relationship between the pitting potential and heating temperature (oxidation temp.) for room temperature pickled 304 stainless steel specimens tested in aqueous solution containing different concentration of chloride ions.

- **Pickling at 60ºC**

Figure 4, presented the recorded pitting potential values for heat tint samples exposed to different chloride concentration after acid pickling at 60ºC for 20min. It can be observed that the pickling at 60ºC improved the pitting potential more pronounced compare when the acid pickling was carried out at room temperature. This improvement was found to depend on the chloride ions concentration.

In general acid pickling at 60ºC has more effective on the pitting potential improvement than the pickling at RT. This improvement was more pronounced for samples tested at chloride concentration up to 1000 ppm Cl⁻.
Heat tint of 304 stainless steel in temperatures range (400, 600, 800 and 1050°C), caused marked reduction in pitting corrosion potential. Heat tint produced at 200 ºC found to improved the pitting potential compared with as received samples as shown in figure 2. This observation can be attributed to the enhancement in the oxide film through the activation of the oxygen reaction with the base metal and hence formation of more coherent passive film enriched with oxygen.

More marked reduction in pitting potential was observed when the samples heated at 400, 600, and 800°C and tested in chloride containing environment. The reduction in pitting potential can be attributed to the localized sensitization within the area adjacent to the grain boundary. At this area the chromium is expected to migrate along with carbon and form intermetallic compound called chromium carbides. Therefore severe pitting corrosion are expected. This because the sensitized area will act as anode and the rest of the area will act as cathode. The anodic area will be distributed on narrow area adjacent to the grain boundaries while the cathodic areas will cover the rest area of the test samples. The severity of the corrosion attack was found to depend on the heat tint temperature as well as the level of the chloride ions, as shown in figure 2. The effect of heat tint on pitting potential was more pronounced for samples heated at 1050°C. This is because of the fact that the chromium is expected to migrate or diffuse out for with oxygen black solid oxide film. Underneath of this oxide film, thin layer of metal surface has lost the most important alloying elements required to combat the corrosion attack namely chromium. Therefore and based on this results severe corrosion attack covering the whole test specimens was resulted. The severity of the corrosion attack, as shown above, found to increase with
increase in the chloride concentration reaching down to -300mv, when tests were carried out in aqueous solution contain of 22,000 ppm chloride ions. Acid pickling compose of aqueous solution contain of 2% HF and 12% HNO₃ at room temperature and 60°C have markedly enhanced the pitting corrosion resistance as shown respectively in figures 3 & 4. Generally, the pickling process of oxidized and/or heat tinted enhance the corrosion resistance due to complete removing of the oxidized or heat affected layer and restore the passive film uniformity and coherency. The most important observation was that pickling at high temperature of 60°C caused better improvement in pitting potential for heated specimens compared to pickling conducted at room temperature. In addition to that, the improvement at 60°C pickling temperature was obtained in shorter time (20 min) compare with pickling process carried out at room temperature for longer duration (200 min), as can be seen in figures 3 & 4.

**Conclusion**

1- Heat tint caused marked reduction in pitting potential particularly when the 304 stainless steel was exposed to temperature above 200 ºC.
2- Heating of 304 austenitic stainless steel at temperature of 200ºC showed slight improvement in pitting potential compare with as received condition.
3- Pickling of heat tinted samples markedly improves its corrosion resistance where marked increase in pitting potentials were obtained. This was found to depend on the pickling time, pickling temperature and oxidation temperature.
4- Pickling at temperature above room temperature (60ºC) found to speed up the pickling process and improve the pitting potential.

**References**

1- C. P. Dillon, Materials Performance, p.62, May 1994