

# Hardening and corrosion behaviour of copper added SUS 304H austenitic steels subjected to thermal cycling

K. K. Alaneme<sup>1,2\*</sup>, U. Ramamurty<sup>2</sup>, O. Bello<sup>1</sup>

<sup>1</sup>Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, PMB 704, Nigeria

<sup>2</sup>Department of Materials Engineering, Indian Institute of Science, Bangalore, 560012, India

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## Abstract

This research was aimed at determining optimum Cu content for the alloy design of SUS 304H austenitic steels having enhanced heat and corrosion resistance. Samples of the steel containing 1, 3, and 5 wt.% Cu were subjected to repeated heating and cooling to a temperature of 760 °C and to a maximum of 15 cycles. Hardness measurement and the corrosion behaviour in 1M NaCl solution were evaluated. The hardness increases with an increase in the number of heating cycles for the three compositions. The hardening response to the thermal cycles is however higher for the 1 wt.% Cu composition and decreases with an increase in the Cu wt.%. The SUS 304H steel containing 3 wt.% Cu exhibited the least susceptibility to corrosion in the 1M NaCl solution irrespective of the number of heating cycles. The SUS 304H steel containing 1 wt.% Cu was found to exhibit the highest susceptibility to corrosion for all heating cycles compared.

Key words: mass loss, SUS 304H austenitic steel, thermal cycles, corrosion behaviour, hardness

## 1. Introduction

The use of Cu alloyed SUS 304H austenitic steels for extreme high temperature applications such as the manufacture of seamless tubes of heat exchangers, and boiler and turbine tubes for ultra super critical coal power generating plant technologies, has continued to generate a lot of research interest [1, 2]. This is due to the excellent high temperature properties (strength, oxidation, corrosion, and creep resistance) derived from the steel, which is processed at low cost and allows for the use of recycled steel scraps rich in Cu. The SUS 304H austenitic steel has a typical composition of Fe-0.1C-18Cr-9.3Ni-0.4Nb-0.2Si-0.8Mn-0.1N (in weight percent) with Cu within the range of 1–5 wt.%. The excellent high oxidation and corrosion resistance of the steel is attributed to its Cr and Ni compositions [3]. Its high creep resistance, mechanical properties and microstructural stability are attributed to the multiple strengthening mechanisms resulting from the refined grain struc-

ture, and the well dispersed NbC(N), Cr<sub>3</sub>C<sub>6</sub>, and Cu nano-precipitates which are developed in the austenitic matrix [4, 5]. Despite the absence of conventional high temperature elements such as Mo, V, W, Ta, the overall high temperature properties of the SUS 304H austenitic steel are comparable to that of the expensively processed Ni based super alloys [6].

Since the difference in composition between the SUS 304H austenitic steel and other austenitic steels in the 304 classification is its Cu content, a number of research investigations have been carried out to understand its contribution in the micro-mechanisms of strengthening of the SUS 304H austenitic steels. Fleury et al. [4] and Wu et al. [7] have shown that nano-sized Cu precipitates which form at high temperatures in the steel help to improve its creep strength. Alaneme et al. [8] have shown that the tensile properties of solution heat-treated SUS 304H are influenced by Cu content but the fracture toughness and fatigue crack growth behaviour are invariant to the amount of Cu in the steel. Sen et al. [9] also reported that anneal-

\*Corresponding author: e-mail address: [kalanemek@yahoo.co.uk](mailto:kalanemek@yahoo.co.uk)

ing treatment on Cu containing SUS 304H austenitic steels does not affect the mechanical performance adversely while still improving the creep resistance.

However, very little has been reported on the influence of Cu on the corrosion behaviour of the SUS 304H austenitic steels. This research work aims to study the influence of Cu wt.% and thermal cycle (resulting from repeated heating and cooling as is observed in the operations of boilers, steam turbines, and other high temperature facilities) on the mechanical stability and corrosion behaviour of SUS 304H austenitic steels containing 1–5 wt.% of Cu. The results from the investigation will help in the ongoing process of selecting optimum Cu content for the design of SUS 304H austenitic steels.

## 2. Materials and method

Three SUS 304H austenitic steels with the nominal chemical composition (in wt.%) of Fe-0.1C-18Cr-9.3Ni-0.4Nb-0.2Si-0.8Mn-0.1N- $x$ Cu, where  $x = 1, 3, \text{ and } 5$ , were examined in this work. The as-cast steel alloys were initially austenized at 1200 °C for 24 h followed by air cooling. They were then forged and rolled at 1200 °C to achieve a 75 % reduction in thickness that was followed by air cooling. Subsequently, the plates were cold rolled to achieve another 30 % reduction in thickness, so that the final thickness of the plates was 10 mm. These cold rolled plates were solution treated at 1200 °C for 30 min followed by water quenching to complete the thermo-mechanical processing [8]. The steels were subjected to a maximum of 15 thermal cycles by repeated heating to 760 °C, holding for 2 h before cooling in air. For each heating cycle, the hardness of the test sample was evaluated using a Rockwell Hardness Tester and following standard procedures in accordance with ASTM E18 – 08b [10]. The corrosion tests were carried out in 1M NaCl solution (which was prepared following standard procedures) on samples representative of 0, 3, 6, 9, 12, and 15 thermal cycles for each composition. The specimens for the test were mechanically polished with emery papers of grit size from 120 to 640. The samples were de-greased with acetone and then rinsed in distilled water before immersion in the 1M NaCl solutions after which were all exposed to atmospheric air. The solution-to-specimen surface area ratio was about 140 ml cm<sup>-2</sup>. The corrosion behaviour of the samples was evaluated by mass loss and corrosion rate measurements in accordance with ASTM G31 standard [11]. Microstructural examination was performed on selected specimens using optical and scanning electron microscopy. The microstructural characterization was performed in accordance with Alaneme [12].

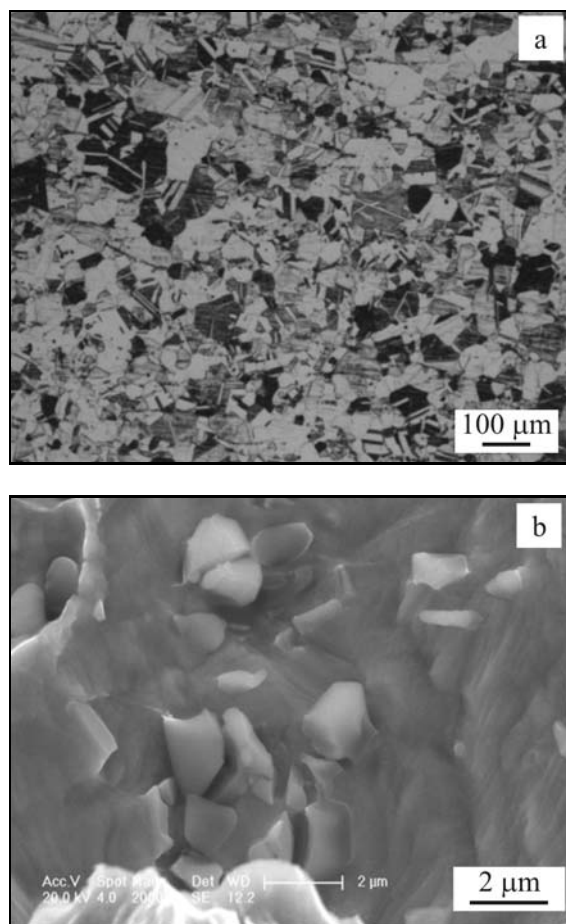


Fig. 1. Representative micrographs showing (a) optical micrograph of the SUS 304H austenitic steel containing 3 wt.% Cu, and (b) scanning electron micrograph of the SUS 304H austenitic steel containing 3 wt.% Cu.

## 3. Results and discussion

### 3.1. Microstructure

Representative optical and scanning electron micrograph of the SUS 304H austenitic steel with 3 wt.% Cu is presented in Fig. 1. The optical micrograph (Fig. 1a) shows recrystallized grains and the presence of significant amounts of annealing twins dispersed in the matrix. Alaneme et al. [8] have reported that the structure observed develops as a result of the thermomechanical processing given to the steel. The scanning electron micrograph (Fig. 1b) confirms that precipitates develop in the steel after it is subjected to thermal cycling. Most of the precipitates observed from the structure were confirmed by EDX analysis to be Cr<sub>23</sub>C<sub>6</sub>. The same microstructural features were observed for other compositions.

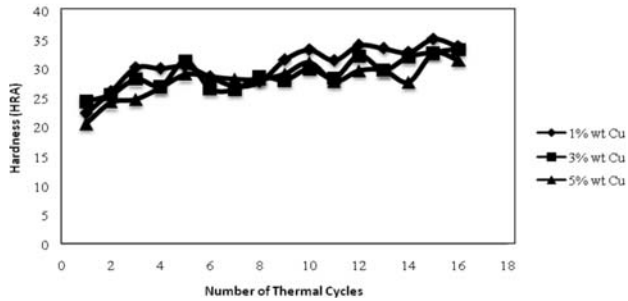


Fig. 2. Variation of the hardness with a number of heating cycles for the SUS 304H austenitic steels.

### 3.2. Influence of annealing cycle on the hardness

Figure 2 shows the graphs of the variation of hardness with a number of heating cycles for the SUS 304H austenitic steel containing 1, 3, and 5 wt.% Cu. It has been observed that there is a general increase in hardness with an increase in the number of heating cycles for the three compositions. This trend is attributed to the precipitation of NbC(N), Cr<sub>23</sub>C<sub>6</sub>, and nano-sized Cu precipitates with an increase in the number of heating cycles. This is an indication that the strength of the steels is not only stable under such thermal operating conditions, but it also improves significantly. The hardening response to the thermal cycles is however observed to be higher for the 1 wt.% Cu SUS 304H and appears to decrease with an increase in the Cu wt.%. Thus it is observed that the 5 wt.% Cu SUS 304H had the least hardening response. It has been reported that during thermal/thermomechanical treatment of Cu containing SUS 304H steels, a reasonable amount of the Cu still remains in solution in the austenitic matrix [8]. It is logical to suggest that the amount of Cu in solution in the austenitic matrix is higher for the 5 wt.% Cu composition. Thus the austenite matrix will be more stable resulting in the precipitation of a relatively lower amount of second phase particles (NbC(N), CrC6). It is noted that for all compositions, there is a drop in the hardening rate between the 4<sup>th</sup> and 8<sup>th</sup> cycle after which the hardening rate increases significantly with increasing number of heating cycle.

### 3.3. Influence of composition on the corrosion behaviour in NaCl solution

Figure 3 compares the mass loss and corrosion rates of the as-received SUS 304H austenitic steels with the three different Cu compositions. It was observed that the 3 wt.% Cu SUS 304H steel exhibited the least susceptibility to corrosion in the 1M NaCl solution. It was also observed from Figs. 4–6 that the

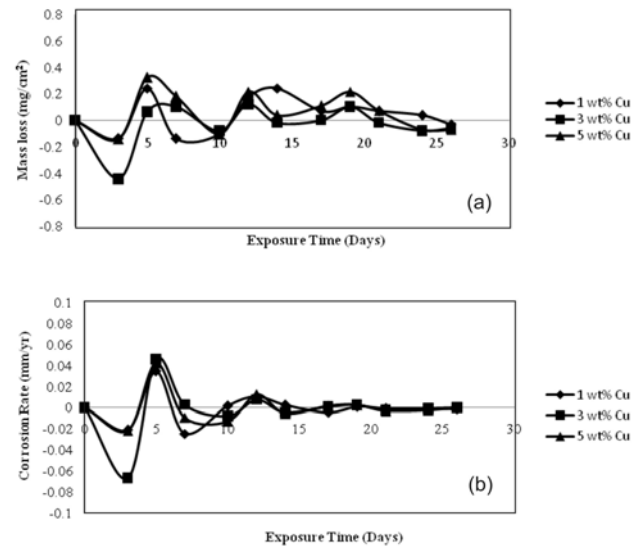


Fig. 3. Variation of the mass loss (a) and of the corrosion rates (b) with exposure time for the as-received SUS 304H austenitic steels in 1M NaCl solution.

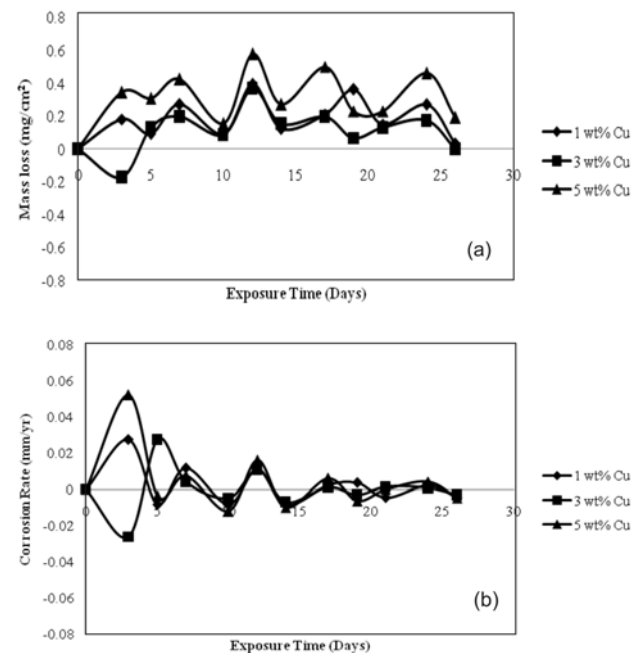


Fig. 4. Variation of the mass loss (a) and of the corrosion rate (b) with exposure time for the SUS 304H austenitic steels subjected to 6 heating cycles in 1M NaCl solution.

3 wt.% Cu SUS 304H for most cases had the least susceptibility to corrosion irrespective of the number of heating cycles. The SUS 304H steel containing 1 wt.% Cu exhibited the highest susceptibility to corrosion for all heating cycles compared. This is an indication that Cu plays a role in the corrosion resistance of SUS 304H austenitic steels, and optimum selection of wt.%

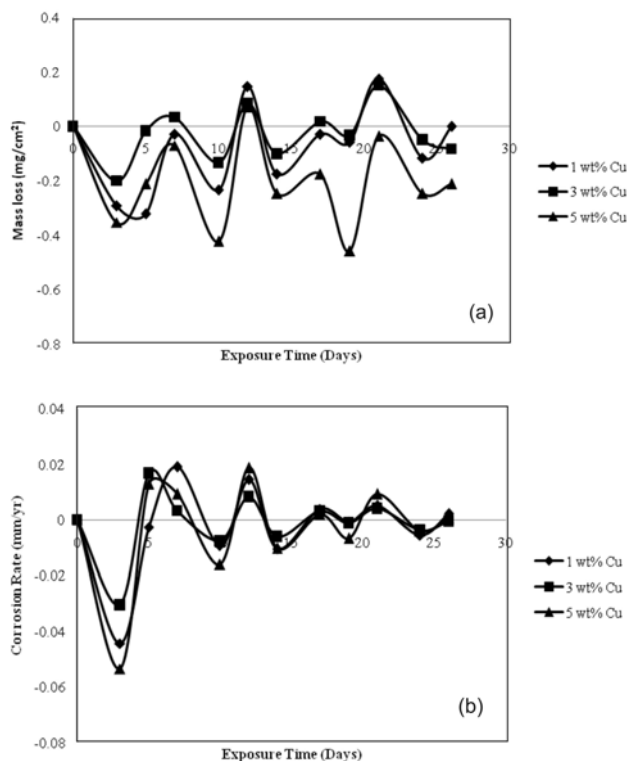


Fig. 5. Variation of the mass loss (a) and of the corrosion rate (b) with exposure time for the SUS 304H austenitic steels subjected to 12 heating cycles in 1M NaCl solution.

Cu in the alloy could lead to further improvements in corrosion resistance. Since the heating temperature of 760 °C is within the sensitization range, there is a greater possibility of chromium segregation to grain boundaries by virtue of the relatively smaller amount of Cu in solution within the austenite matrix for the 1 wt.% Cu composition. Thus the SUS 304H steel containing 3 wt.% Cu steel appears to be the most corrosion resistant composition in NaCl solution.

Figure 3b shows that the alloys have generally good corrosion resistance, as it is observed that the maximum corrosion rate for the entire period of exposure is less than 0.06 mm/yr for all compositions of the SUS 304H steel.

It is observed that with the exception of samples subjected to 6 heating cycles, the mass loss and corrosion rate reduce with increasing number of heating cycles. It is observed from Figs. 5a and 6a that the oxide film formed on the samples is more stable (as reflected by the negative mass loss which is indicative of weight gain due to oxide film formation) in comparison with Fig. 3a [13, 14]. This observation is supported by the corrosion rate plots (Figs. 5b and 6b), where it is seen that the maximum corrosion rates are less than 0.03 mm/yr in comparison to those of the as-received samples which had maximum corrosion rates of above 0.05 mm/yr.

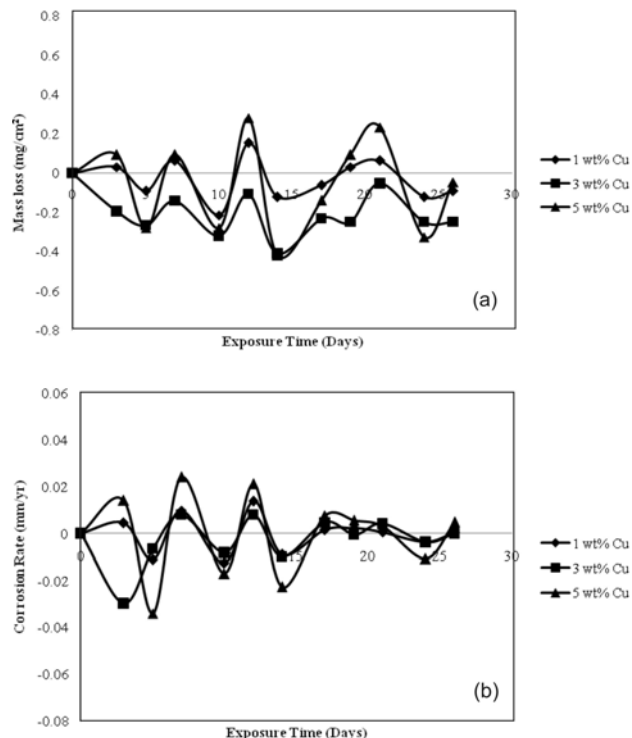


Fig. 6. Variation of the mass loss (a) and of the corrosion rate (b) with exposure time for the SUS 304H austenitic steels subjected to 15 heating cycles in 1M NaCl solution.

### 3.4. Effect of annealing cycles on corrosion behaviour

Figures 7–9 present the variation of mass loss and corrosion rates with the number of heating cycles for each steel composition. From Fig. 7a it is observed that for the 1 wt.% Cu, the mass loss increases with an increase in heating cycles attaining a peak after 9 heating cycles. The mass loss reduces significantly from the 12<sup>th</sup> to 15<sup>th</sup> heating cycle. For the 3 wt.% Cu, it is also observed that peak corrosion is attained after 6 heating cycles (Fig. 8a). Further heating cycles resulted in a significant reduction in corrosion susceptibility as is observed from between the 7<sup>th</sup> to 15<sup>th</sup> cycle. It was observed that the sample subjected to 15 thermal cycles presented the least susceptibility to corrosion in NaCl solution. The same trend is observed for the 5 wt.% Cu SUS 304H austenitic steel (Fig. 9), in which peak corrosion susceptibility was attained for 6 heating cycles. In the case of the 3 wt.% Cu SUS 304H steel, it is observed that after the 6<sup>th</sup> annealing cycle the corrosion susceptibility reduces with further increase in the number of heating cycles.

## 4. Conclusions

The influence of weight percent Cu additions and

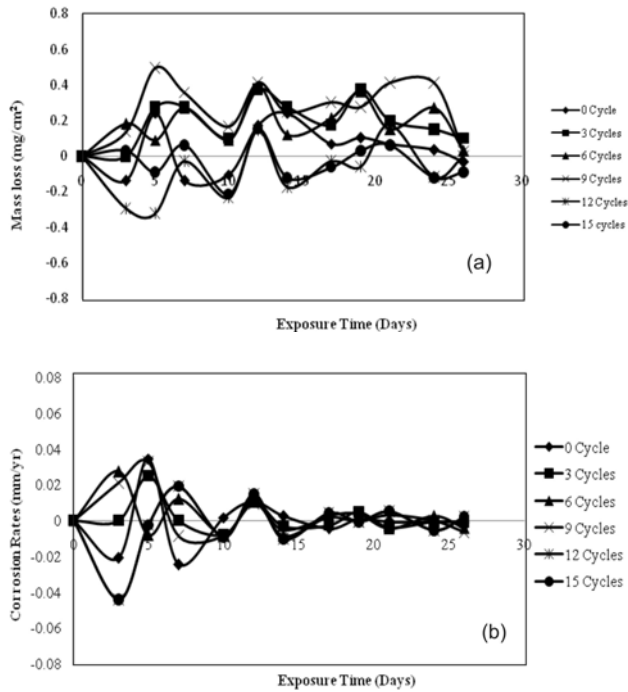


Fig. 7. Influence of the number of heating cycles on the mass loss (a) and on corrosion rate (b) of SUS 304H austenitic steel containing 1 wt.% Cu in 1M NaCl solution.

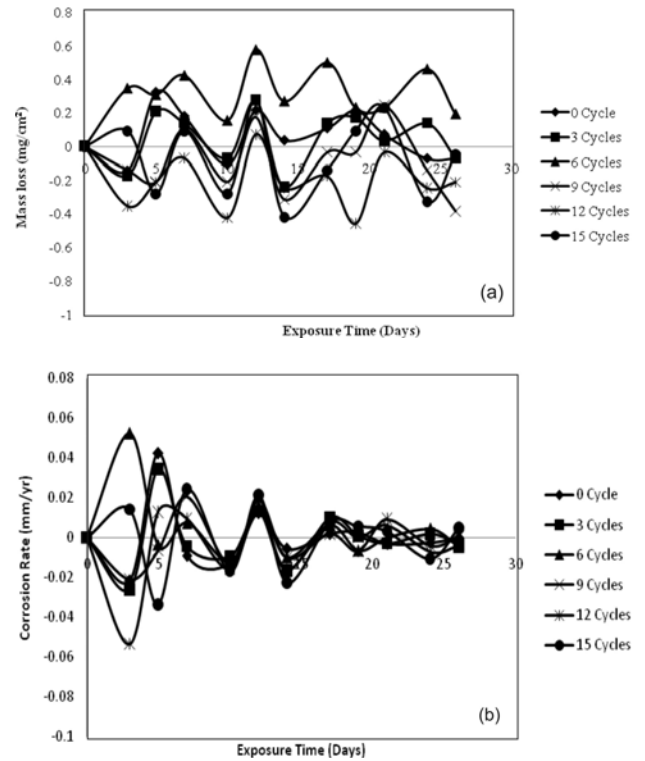


Fig. 9. Influence of the number of heating cycles on mass loss (a) and on corrosion rate (b) of SUS 304H austenitic steel containing 5 wt.% Cu in 1M NaCl solution.

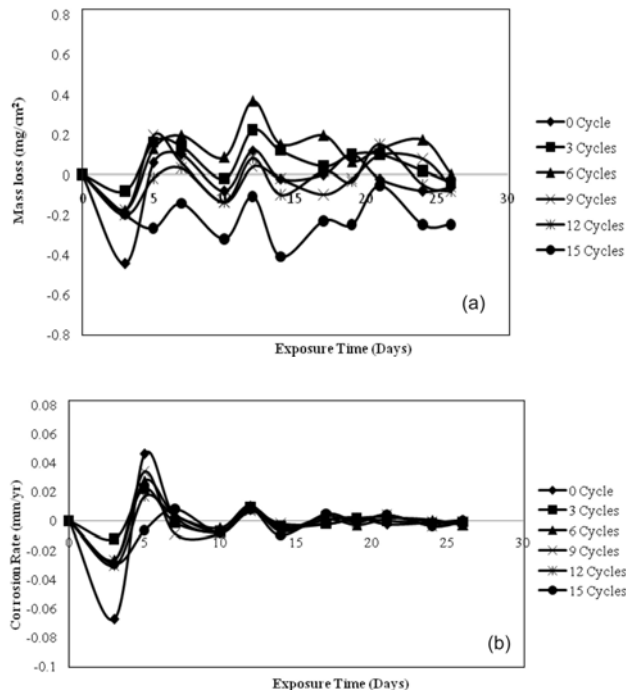


Fig. 8. Influence of the number of heating cycles on mass loss (a) and on corrosion rate (b) of SUS 304H austenitic steel containing 3 wt.% Cu in 1M NaCl solution.

thermal cycling at 760°C on the hardness and corrosion behaviour of SUS 304H austenitic steels has been

investigated. From the results and discussion, the following conclusions are made:

1. There is a general increase in hardness with an increase in the number of heating cycles for the three steel compositions. The hardening response to the thermal cycles is however observed to be higher for the 1 wt.% Cu composition and appears to decrease with an increase in the Cu wt.%.

2. The 3 wt.% Cu SUS 304H steel exhibited the least susceptibility to corrosion in the 1M NaCl solution irrespective of the number of heating cycles. The 1 wt.% Cu containing SUS 304H steel exhibited the highest susceptibility to corrosion for all heating cycles compared.

3. The corrosion susceptibility of the three compositions attains a peak between the 6<sup>th</sup>–9<sup>th</sup> cycle, after which there is a significant reduction in corrosion rate with further increase in heating cycle.

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