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# Pitting corrosion of cold rolled solution treated 17-4 PH stainless steel

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ABSTRACT

In the present paper the effects the of cold rolling on pitting corrosion of 17-4 precipitation hardening stainless steel in 3.5 wt% NaCl solution was investigated. In order to clarify the effect of cold rolling the metastable pitting has been examined in more details. The results presented show that cold rolling increases the dissolution rate of metastable pitting in a manner which facilitates the transition from metastable to stable pitting. On the other hand, the frequency of occurrence of metastable pits decreases with cold working. In overall, cold rolling has no significant effect on pitting potential.



## 1. Introduction

The plenitude of applications has made the stainless steels important classes of alloys. For many applications, stainless steels are subjected to different levels of cold working during the final steps of manufacturing. In practical point of view, beside of the corrosion resistance, the mechanical properties of stainless steels are of interest. In the annealed state, yield strength of austenitic stainless steels is relatively low. Higher yield strength and tensile strength can be achieved through cold working process. Such improvement in mechanical properties by plastic deformation generally accompanies with microstructural changes like increasing dislocations density, introducing deformation bands, twining, and more importantly for austenitic stainless steels, deformation induced martensite [1–3]. Microstructure is one of the most important metallurgical aspects of localized corrosion of stainless steels. So that, the influence of cold working on corrosion resistance of stainless steels has been subject of several studies [1–10]. However, no comprehensive model has been proposed on the influence of cold plastic deformation on localized corrosion of stainless steels. While it has shown that cold rolling decreases the pitting potential of austenitic stainless steels [2,3,5,10], on contrast, increase in pitting potential of work-hardened stainless steel has also been observed [7]. Higher passive current and lower protection potential have been reported for cold worked stainless steels. It is also mentioned that pit propagation takes place easier for the work-hardened material [2,3]. However, lower passive current and more noble protection potential has been observed for the cold rolled stainless steel [7].

For an austenitic stainless steel, it has been shown that the number of pits generally increases with increasing pre-deformation. Moreover, the rate of pit growth increases even after small deformation (1%) but more severe deformation has little additional effect [10]. Both the thickness and Cr:Fe ratio of passive film on AISI 304 stainless steel increase as a result of cold rolling procedure. X-ray diffraction has shown a texture for cold rolled material, which enhances diffusion of Cr into the passive film over the surface and therefore, increases pitting resistance [7]. Susceptibility to pitting for AISI 304 stainless steel in chloride containing sulfate media was reported to be greater for cold worked than annealed sample. The in situ microscopic observation has showed that pit initiation began at defective interfaces. The passivity decay with cold rolling appeared to be mainly due to the formation of defective interfaces [2].

It has been reported that prior deformation accelerates the sensitization of stainless steels. Plastic deformation induces slip bands, which are prime sites for carbide precipitations. Cold working promotes the formation of both grain boundary and intragranular $Cr_2N$ precipitates of a high-nitrogen stainless steel. On the other hand, desensitization was shown to be faster in highly cold worked material, especially at high temperatures [6,9].

Among microstructural changes occur during cold working, modification of non-metallic inclusions has an important role in both strip quality and corrosion resistance. Cold working may produce and elongate the inclusions or produce micro-cracks at the interface of matrix–inclusion, which affects the pitting resistance of stainless steel [11,12].

Passivity break down, which plays an important role in initiation of localized corrosion of stainless steels, is a phenomenon showing a statistical and probabilistic nature [13,14]. Even at controlled laboratory conditions, passivity breakdown exhibits a wide

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scatter of initiation time and/or location on the electrode surface. Therefore, the pitting potential may not be considered as a unique value determined for a given combination of material and environment. Although the importance of the probabilistic nature of the potential at which a stable pit forms has been well acknowledged, to our knowledge, no attempt has been made so far to employ statistic/stochastic approaches to pitting phenomena in matter of cold worked stainless steels. Assessment of the influence of cold working on the pitting corrosion by using statistical approach may lead to more in-depth understanding.

The 17-4 PH stainless steel is one of most common types of precipitation hardening stainless steels. The combination of high strength and ductility together with moderate corrosion resistance has made this steel an attractive material for designers [15–19]. In the present investigation the effect of cold rolling on pitting corrosion of solution treated 17-4 PH stainless steel in 3.5 wt% NaCl solution was studied. Although this stainless steel is not used in solution treated condition, however, it is still worth to study the influence of cold working on its pitting corrosion susceptibility. Attempt has been made to explain the effect of cold working using statistical approach with emphasis on pitting initiation.

## 2. Experimental

### 2.1. Material and cold rolling

The 17-4 PH (UNS S17400) stainless steel was supplied by EICO, Esfarayen, Iran. The material was received as a hot rolled billet with diameter of 90 mm. The alloy composition is given in Table 1. Discs with 5 mm thickness were obtained from the billet and were solution treated at 1050 °C for 1 h and then were water quenched. By this solution heat treatment the previous Cu-rich precipitates dissolve and the martensitic matrix supersaturates with Cu and Cr [17]. Solution treated discs were subjected to cold rolling leading to 10%, 30%, 50% and 70% final reduction of thickness. For the rest of the paper, specimens are denoted as ST for solution treated, 10%, 30%, 50% and 70% for 10%, 30%, 50% and 70% cold rolled specimens, respectively. 10 mm × 10 mm specimens were cut from the rolled discs, with test surfaces parallel to the rolling direction. Then the specimens were mounted into epoxy resin, polished up to diamond finish (1 μm), and etched in modified Fry's reagent to reveal the microstructural changes due to the cold rolling [20]. Microstructure of the solution treated and the cold rolled samples was examined using optical microscopy and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometry (EDX).

### 2.2. Potentiodynamic experiments

Potentiodynamic experiments were carried out in three-electrode cell at two different potential scan rates of 30 and 5 mV/min in 3.5 wt% NaCl solution. Higher potential scan rate was employed to investigate the effect of cold rolling on pitting potential, and slower potential scan rate was used to study the nucleation frequency of metastable pitting as a function of cold working. The electrochemical cell was a 250 ml beaker open to air. A saturated Calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode were used. The exposed surface area of 0.5 and 0.2 $cm^2$ was prepared for the higher and lower potential scan rates, respectively. The electrodes surface was prepared by grinding up to 1200 grit SiC paper. For all experiments, the polarization started after 15 min recording corrosion potential, which was enough to approach steady state condition. All experiments were performed at room temperature, and were repeated 15 times at higher potential scan rate and 5 times at lower potential scan rate.

### 2.3. Potentiostatic experiments

To study pit nucleation, potentiostatic experiments were carried out at constant potential of 0 V/SCE. Surface area of 0.2 $cm^2$ of each sample, which was finished with 1200 grit SiC paper, was exposed to the 3.5 wt% NaCl solution open to air. Such surface area was chosen to reduce the overlap of events. Before the test beings run, open circuit potential was measured for 15 min, and then current response of the sample at constant potential was recorded at frequency of 50 Hz for 1200 s. All experiments were carried out at room temperature and were repeated 5 times for each specimen.

## 3. Experimental results

### 3.1. Microstructure

Fig. 1 shows the microstructure of 17-4 PH stainless steel after solution heat treatment at 1050 °C for 1 h. The microstructure was composed mainly of martensite and minor fraction of δ-ferrite (less than 1%). It has been shown that the martensite at this condition consists of lath structure containing very high density of dislocations [17]. No evidence of Cu-rich precipitates in the matrix has been observed in the solution treated condition and it is believed that the martensite is supersaturated with Cu and Cr [16,17]. The absence of δ-ferrite in the microstructure allows considering the effect of cold rolling only on the martensite phase.

Fig. 2a shows SEM micrograph of an inclusion in specimen 10%. The EDX analysis, Fig. 2b, indicates that the inclusion is sulfide type and contains Fe and Cr. When the steel is subjected to cold deformation, because the non-metallic inclusions and the steel matrix have different ductility, the applied strain creates a trench at the interface of matrix and inclusion. Such trench is shown in Fig. 2c and d for specimens 50% and 70%, respectively. By increasing the cold working the fracture at the interface has occurred more severely. In specimen 70%, for example, the inclusion is nearly debonded from the matrix. Beside the inclusion, Fig. 2c shows some spherical precipitates. The EDS analysis has indicated that they are Nb-rich phases and are believed to be NbC carbides [21].

### 3.2. Pitting potential

Typical potentiodynamic polarization curves obtained in 3.5% NaCl solution at 25 °C for different specimens are depicted in Fig. 3. As it can be seen, cold rolling did not noticeably influence the corrosion potential and the passivity current density. Since pitting potential ($E_{pit}$) has a probabilistic character [20], it is reasonable to employ statistical approach to address the effect of plastic deformation on $E_{pit}$.

Fig. 4 shows the cumulative probability of pitting potential distribution for 17-4 PH stainless steel with different cold rolling reductions determined from potentiodynamic polarizations. The

**Table 1**
Chemical composition (in weight percent) of 17-4 PH stainless steel.

| C | S | P | Si | Mn | Cu | Ni | Cr | V | Nb | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.04 | 0.012 | 0.018 | 0.32 | 0.61 | 4.14 | 4.59 | 15.09 | 0.013 | 0.358 | 0.18 | Bal. |