Pitting susceptibility of AISI 304 stainless steel after cold rolling

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Abstract

The austenitic grade AISI 304 stainless steel is traditionally employed for processing equipment in chemical plants due to its relatively good corrosion resistance and mechanical stability. However, it is susceptible to pitting corrosion due to chloride attack which can lead to catastrophic failures during operation. Cold rolling of the metallic sheets used to construct equipment such as tanks and pressure vessels can further aggravate the situation by increasing the material's susceptibility to localized corrosion. In this work the pitting corrosion resistance of cold rolled AISI 304 stainless steel plates was assessed using chronoamperometric curves and potentiodynamic polarization curves. Cold rolling was performed in a two-roll mill at room temperature, achieving thickness reductions ranging from 10% to 70%. The presence of pits on the surface of the samples was assessed using optical microscopy. The onset of pitting corrosion was closely related to the strain level of the rolled plates. There was a steep decrease of resistance to localized attack as the thickness reduction increased.

Keywords: 304 stainless steel; cold rolling; pitting corrosion

Introduction

AISI 304 stainless steel is widely used as structural components and chemical processing equipment due to a suitable combination of mechanical strength and corrosion resistance (1). However, it is well known that it is prone to pitting corrosion in chloride-containing environments (2,3). Pitting corrosion results from both metallurgical and electrochemical factors. Properties of the passive film such as conductivity, structure and composition are also important to the stability of the passive film (4). The main metallurgical factors affecting the pitting corrosion resistance of stainless steels are grain size, alloy composition, sensitization, presence of second phase particles and non-metallic inclusions (4). Furthermore, cold working is also reported to influence the onset of pitting corrosion of stainless steels. Mudali et al. (5) investigated the effect of cold rolling on the corrosion resistance of N-bearing 316L stainless steel in a neutral chloride solution. They observed that cold working up to 20% increased the pitting resistance whereas a decrease was observed for higher deformations. Lu et al. (6) have found that strain percentages of up to 10% presented a more profound effect on the pitting potential of AISI 304 stainless steel whereas pitting susceptibility was little affected by more

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intense strains. Phadnis et al. (7) observed that rolled AISI 304 stainless steel with 66% cold work presented enhanced resistance to pitting corrosion to the higher Cr:Fe in the passive film. This was attributed to the easier diffusion of chromium through oriented grains in the cold worked steel. Some authors reported that cold working did not affect the pitting potential of stainless steel. Thus, in spite of several scientific investigations, the role of cold working on the pitting corrosion behavior can be considered still unclear.
Cold working yields dislocation networks, twins, deformation bands, strain-induced martensite in austenitic stainless steels (8). These structural features can affect the pitting corrosion resistance of these materials (9,10). Since cold working is a common manufacturing operation of stainless steels, it is of prime interest to gain knowledge about its effect on the susceptibility of these materials to pitting corrosion. This interest is even more reinforced if one thinks about the contradictory reports found in the literature. In this respect, the present work aimed at investigating the susceptibility of AISI 304 stainless steel to pitting corrosion after cold working. The samples were rolled up to thickness reductions of 70%. Corrosion tests were comprised of chronoamperometric and potentiodynamic polarization measurements. The pit morphology was observed by optical microscopy.

Methodology

The nominal chemical composition of the commercial AISI 304 stainless steel plate used in this investigation is reported in Table 1. The dimensions of the specimens were 125 mm x 100 mm x 4 mm.

Table 1. Nominal chemical composition (wt%) of the AISI 304 stainless steel used in this investigation.

C (max)	Si (max)	S (max)	P (max)	Mn (max)	Cr	Ni	Fe
0.08	0.75	0.03	0.04	2.0	18.0-20.0	8.0 – 11.0	Bal.

The as-received samples were initially solution-treated at 1000 ºC for 1 h in a resistive furnace and water-quenched to guarantee an initial homogeneous condition. Next, the samples were cold worked in a twin roll mill. Thickness reductions of 10% up to 70% were achieved by cold rolling at room temperature.
The susceptibility to pitting corrosion was assessed by electrochemical tests. The working electrodes were prepared by embedding the samples into cold curing epoxy resin. The samples were prepared by mechanical grinding with progressively finer SiC paper up to 1000 grit size. The measurements were performed with an Autolab PGSTAT 100 potentiostat/galvanostat. The electrochemical cell consisted of a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as reference and a platinum wire as counter-electrode. All potentials mentioned in this work are referred to the SCE. The electrolyte consisted of a NaCl 3.5 wt.% solution at room temperature. An initial stabilization step was conducted with the working electrodes remaining immersed for 1 h in the electrolyte before being polarized. This procedure was used for obtaining the potentiodynamic polarization curves and chronoamperometric curves.
Potentiodynamic polarization curves were obtained in the potential range between -300 mV versus the open circuit potential (OCP) up to 1 V versus the OCP at a scanning rate of 1 $mV.s^{-1}$. Chronoamperometric curves were obtained at a static potential of -50 mV. The

current density was monitored during 30 minutes at this potential. The presence of corrosion pits was assessed using optical microscopy (Olympus).

Results and Discussion

Potentiodynamic polarization curves of the AISI 304 stainless steel samples with different thickness reductions by cold rolling are shown in Fig. 1. The electrochemical parameters determined from these curves are displayed in Tab. 2. The polarization curves indicate that the as-received material has the widest passive range. The breakdown potential (E_b) denoted by the sharp increase of the current density at a specific potential is clearly lower in the cold worked samples.

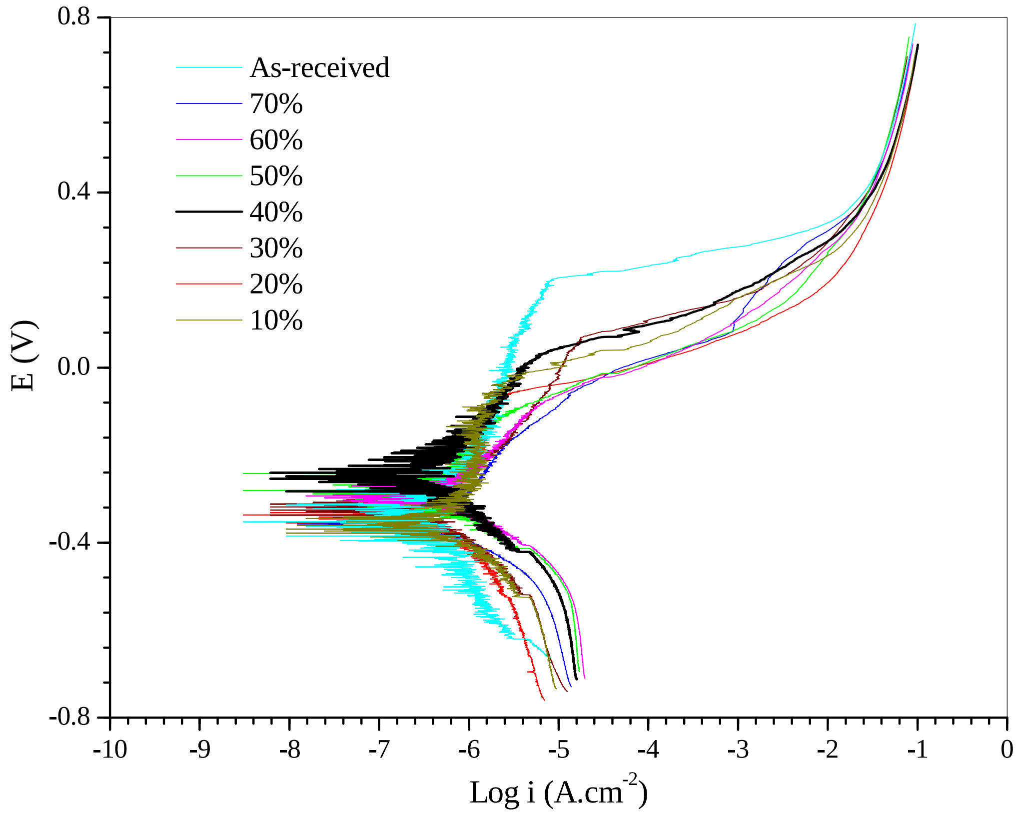

Figure 1. Potentiodynamic polarization curves of the AISI 304 stainless steel samples with different thickness reductions.

The breakdown potential (E_b) was severely affected by the cold working degree. It is seen from Table 2 that the E_b of the as-received material was far higher from those obtained for the cold worked samples. Moreover, the passive range was found to decrease for progressively higher thickness reductions. The most accentuated shortage of the passive range occurred from a thickness reduction of 40% up to 70%. Moreover, the data point to higher corrosion current densities (i_{corr}) in this same cold working range, suggesting that the general corrosion of the AISI 304 stainless steel is also negatively affected by the deformation imparted by cold rolling. However, the influence on i_{corr} was not as marked as that observed on the pitting corrosion susceptibility of the alloy. It was not possible to identify a clear trend regarding the variation of the corrosion potential (E_{corr}) with the cold working degree.

Table 2 - Electrochemical parameters determined from the potentiodynamic polarization curves shown in Figure 1.

Thickness reduction	E_{corr} (mV)	i_{corr} ($\mu A.cm^{-2}$)	E_b (mV)	Passive range (mV)
As-received	-339	0.26	204	344
10%	-366	0.39	-12	251
20%	-347	0.34	-50	183
30%	-314	0.31	73	195
40%	-247	0.36	33	153
50%	-290	0.41	-97	123
60%	-296	0.58	-26	164
70%	-349	0.53	-160	112

According to Mudali et al. (4) the increased pitting corrosion susceptibility of cold worked austenitic stainless steels is related to the higher concentration of pitting sites such as deformation bands formed during dislocation glide. In this respect, the data shown in Table 2 suggest that even the least deformed samples (up to 30%) manifest this effect.

Chronoamperometric curves of the AISI 304 stainless steel samples with different cold working degrees are shown in Fig. 3. The current densities are higher for the most deformed samples which agree with the results obtained from the polarization tests. It is noteworthy that the chronoamperometric curves referred to the as-received material presents a steady state, denoting a stable current density evolution throughout the whole test. Furthermore, the current densities of the as-received material remained low during the test. This effect is probably related to the high breakdown potential of this condition with comparison with the cold worked samples. A gradual increase of the current densities is perceived from 10% to 30%. From 40% and beyond the current densities increase, especially for the samples rolled up to thickness reductions of 50%, 60% and 70%. For these samples the variation of the current density with time is less homogeneous. Moreover, the current density increases at a higher rate, suggesting that the stability of the passive film decreases for the most deformed samples.

In order to give visual indications about the effect of cold working on the pitting corrosion susceptibility of the AISI 304 stainless steel, the samples were inspected by optical microscopy after the potentiodynamic polarization tests. Representative micrographs of the AISI 304 stainless steel with different cold working degrees after the polarization tests are shown in Fig. 4. Presence of localized attack was seen on the surface of all samples independent of the cold working degree. Even the as-received sample has signs of localized attack on its surface, as it was also observed in the potentiodynamic polarization curves shown in Fig. 1. However, the attack becomes more aggressive from the thickness reduction of 40% up to 70% (Fig 4e to 4g).

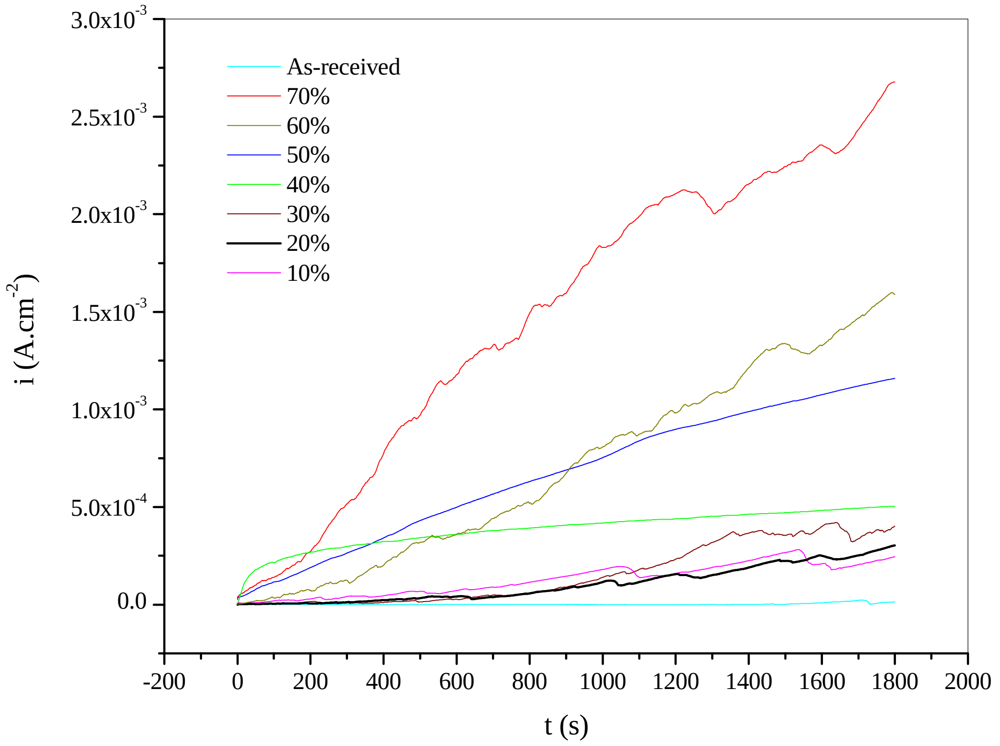

Figure 3. Chronoamperometric curves of the AISI 304 stainless steel samples with different thickness reductions.

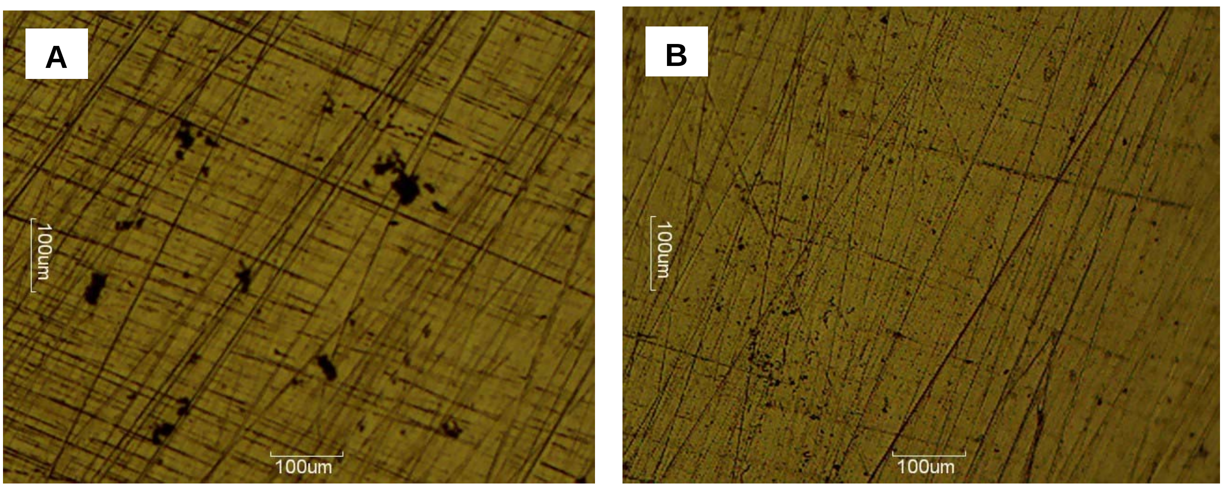

Figure 4. Optical micrographs of the AISI 304 stainless steel with different cold working degrees after the polarization tests: a) As-received; b) 10%; c) 20%; d) 30%; e) 40%; f) 50%; g) 60%; h) 70%.

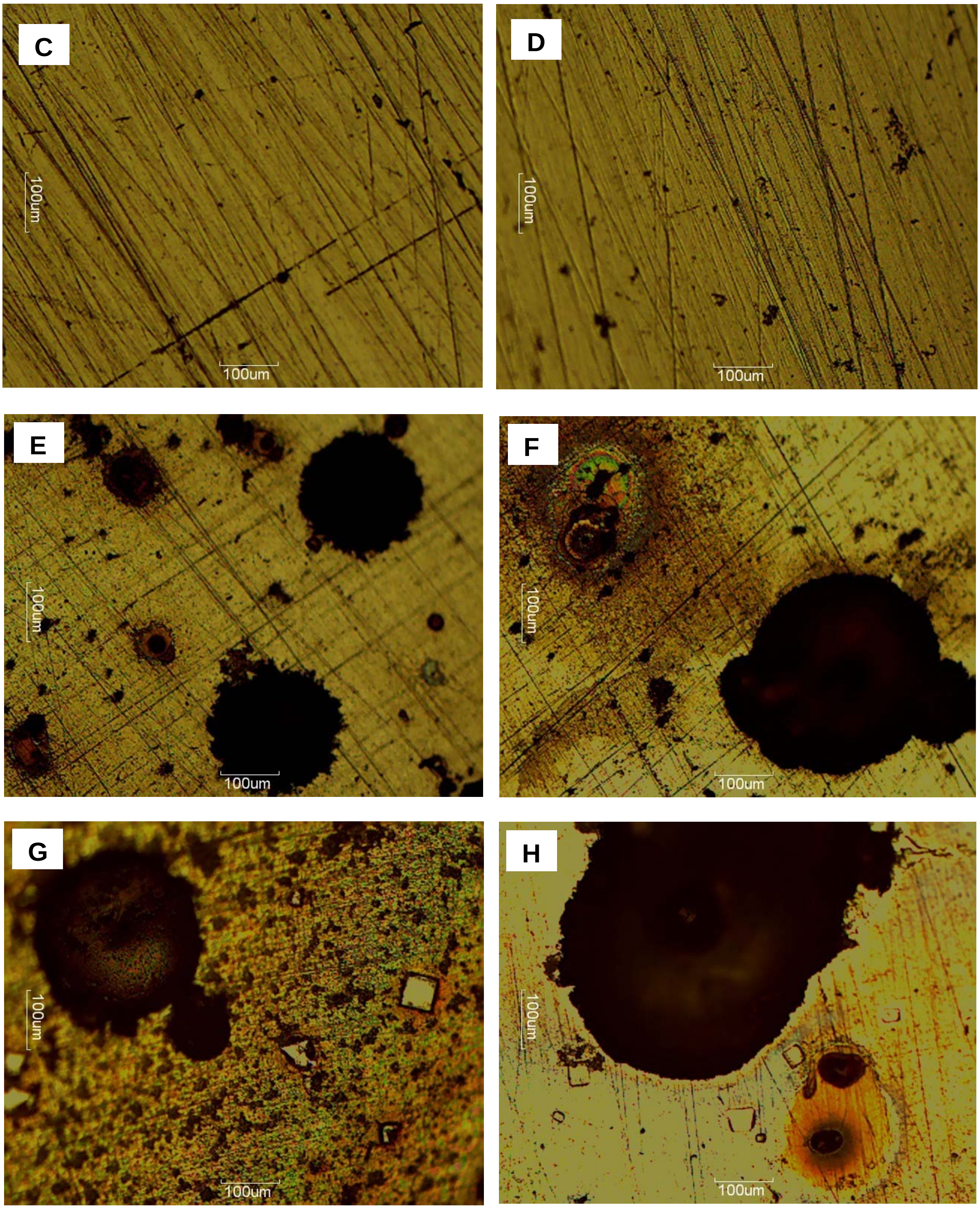

Figure 4. Continued.

Conclusions

The AISI 304 stainless steel was susceptible to pitting corrosion under the experimental conditions employed in this work. The thickness reduction imparted by cold rolling strongly affecting the resistance to localized attack. The results showed that the susceptibility to pitting corrosion, increased with the cold working degree. Higher deformation led to a shortage of the passive range as well as a decrease of the breakdown potential. Chronoamperometric curves revealed that the current densities increased for the most deformed samples, suggesting that the passive film became progressively less stable with the cold working degree.

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