Effect of Plastic Deformation on the Corrosion Behavior of Super1Duplex Stainless Steel

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Abstract: The effect of plastic deformation of super duplex stainless steel on the subsequent corrosion behavior in 3.5% sodium chloride solution was investigated. Potentiodynamic corrosion measurements were conducted at temperature of 90°C. Deformation at levels of 8 and 16%plastic strain showed high intensity of deformation bands. The presence of such deformations was highly sensitive to corrosion attack in the tested environment. The results confirmed the significant effect of deformed surfaces, as the plastic deformation level increased the corrosion resistance of super duplex stainless steel decreased.

Keywords: Super duplex stainless steel, Plastic deformation, Potentiodynamic

INTRODUCTION

Duplex stainless steels have become more attractive than single phase austenitic and ferritic grades in many applications owing to their high strength and corrosion resistance in chloride containing media. Like other stainless steels this alloy relies on surface passive films for their excellent corrosion resistance. The fine austenite-ferrite microstructure of these materials promotes an excellent combination of toughness and mechanical resistance, desirable for many applications in the chemical and petrochemical industries (Tavares, *et al* 2005). Plastic or cold deformation is invariably present in components used in plant due to fabrication techniques used in machining, bending and rolling. Stress present due to cooling from high temperatures during welding and welding in constrained geometries cause deformation in materials and high stress/strains (Kain, *et al* 2004). Cold working generally introduces deformation substructures like dislocation networks, twins, deformation bands, cell structures and emerging slip steps at thesurface (Kamachi, 2000). Structure transformation, which occurs in metals under plastic deformation bycold work, is accompanied by considerable changes in the most important physical andmechanical properties. Crystal defects, metallurgical structure, and composition affect the properties of the protective passive films, such as thickness, strength solubility, and porosity,and hence the susceptibility to localized breakdown and pitting of the alloy (Barbucci, 2002).

Stainless steels are fit for cold work and mechanical treatment, allowing controlled modulation of the mechanical resistance, but corrosion properties can be modified in an uncontrolled way. The corrosion resistance of stainless steels can be significantly affected by metallurgical parameters such as cold working, alloy composition, inclusions, heat treatment, sensitization, precipitation (Hamad, 2006). It has been reported that structure nonhomogeneity encourages localized corrosion of passivable metals. In particular, the detrimental effect of plastic deformation on the corrosion resistance of stainless steel has been shown. Thus, cold working has been found to lower the critical pitting potential of austenitic stainless steel in 0.1M HCl and in solution simulating seawater (Barbucci, 2002).There are studies reporting detrimental influence of cold work on the pitting corrosion resistance of AISI 304 (18Cr-8Ni), 316L (17Cr-12Ni-2Mo) and 301 (17Cr-7Ni) type austenitic stainless steels (Hamad, 2006); Mazza,1979).

In duplex stainless steels and due to the presence of a massive second phase during processing makes deformation more complicate and the microstructure is a decisive limiting factor of plastic behavior. In addition to the work hardening and softening mechanisms required to deform each phase, the ferrite/austenite boundaries play an important

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role in duplex microstructure; the accommodation of macroscopic deformation depends on plastic characteristics of both phases (Reis, 2000). When the ferrite and austenite phases in duplex stainless steel are jointly deformed, the distribution of strains among the phases is no longer uniform. When straining begins in duplex stainless steels, strain concentrations appear in the softer ferrite (Reis, 2000). As deformation increases, strain gradients may decrease as a result of accommodation mechanisms such as recovery and recrystalization, cracking formation, as well as interphase and grain boundary sliding. On cold working strain induced martensite and residual stress are significantly introduced on the surface, which affects the localized corrosion resistance by increasing the number of active anodic sites on the surface. Thus it is the aim of this paper to discuss the effect of the associated substructural development of the two phases of ferrite and austenite on corrosion resistance of duplex alloy.

SAMPLES AND TEST PROCEDURES

The chemical composition of the investigated super duplex stainless steel in weight percentage is 0.02%C, 24.84%Cr, 6.54%Ni, 0.45%Mn, 2.07%W, 0.34 % Si , 3.10%Mo, 0.28%N and the rest is iron. The as-received specimens were solution annealed at 1050ºC for 1 hour and water quenched. Specimens were machined in cylindrical tensile shape of 100mm length and 5mm diameter; a specimen schematic view is showing in Fig. 1. Before straining, specimens were mechanically polished starting with coarse grain emery paper of 200, 400, 600, 800 and 1200 and then followed by alumina paste in order to get a mirror like surface, then rinsed with acetone and dried by hot air. Specimens were strained in axial tension to the required plastic strain percentage at a constant rate of 0.2mm/min using a tensile test machine. Metallographic observation using optical and scanning electron microscopy was carried out on strained and unstrained specimens after electrochemical etching in 10% oxalic acid solution.

After straining, electrochemical corrosion behaviour of the specimens was investigated using potentiodynamic polarization measurements in 3.5% sodium chloride according to ASTM G 5. The electrochemical cell was a conventional three electrode cell comprises the working (specimen), the reference electrode silver / silver chloride (Ag/AgCl) and platinum counter electrode. All electrochemical measurements were made at temperature (90°C) using **Princeton Potentiostat/Galvanostat (263A)**. Before potentiodynamic measurements, the electrodes were immersed in a glass corrosion cell filled with 700ml of the investigated electrolyte. The open circuit potential became stabilized after 30min. The potentiodynamic curves measurement were recorded at a potential scan rate of 1 mV /s starting from 100Mv below the open-circuit potential (OCP). The potential scan continued while the corrosion current density was monitored. Analysis from the polarization curves were made to determine the breakdown potential at which the current increased with time and exceeded 1mA.

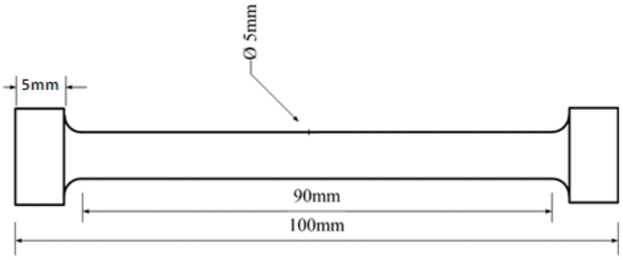

Fig. 1. Schematic of the test specimen.

LABORATORY OBSERVATIONS

Surface Texture: The morphology of the surfaces after straining was carefully examined using scanning electron microscopy (SEM). Examples of unstrained and strained surfaces texture are shown in (Fig. 2a-c). It can be seen that the unstrained specimen has uniform texture as shown in Fig. 2a. In the case of deformation, the deformed textures are composed of elongated grains and shear bands crossing the grains. The presence of shear bands was found on 8% and 16% strained specimens, (Figs. 2b & c). However, the percentage of shear bands is higher in the specimen strained to 16% (Fig. 2c).

Etched Surface Texture: Samples after straining were polished to mirror for metallographic examination. By contrast on the oxalic acid etched surfaces shown in Fig. 3(a, b), there was a significant difference between undeformed and deformed surfaces on ferrite (a) and austenite (g) grains. Change in surface texture at ferrite phase (a) when deformation conducted at 16% plastic strain is shown in (Fig. 3b).

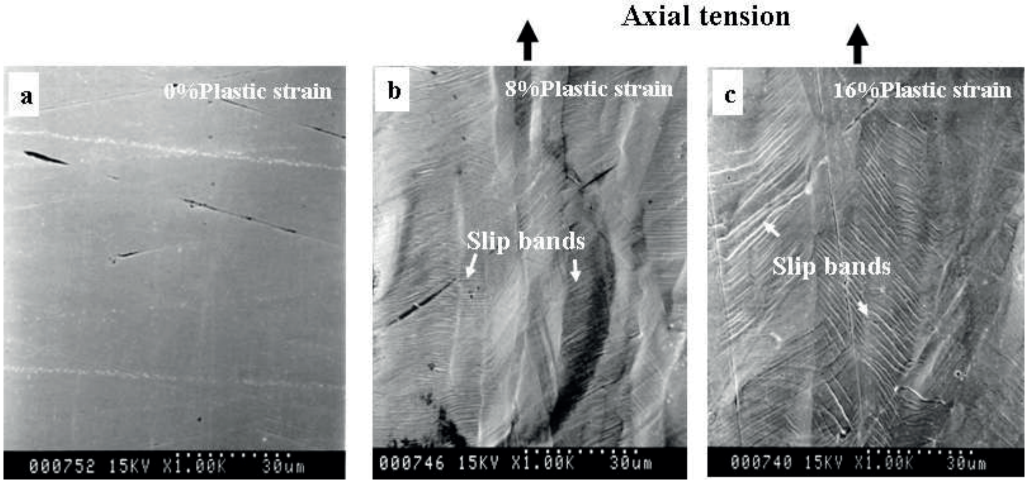

Fig. 2. SEM photographs of unstrained, 8% and 16% plastic strain super duplex alloy surfaces.

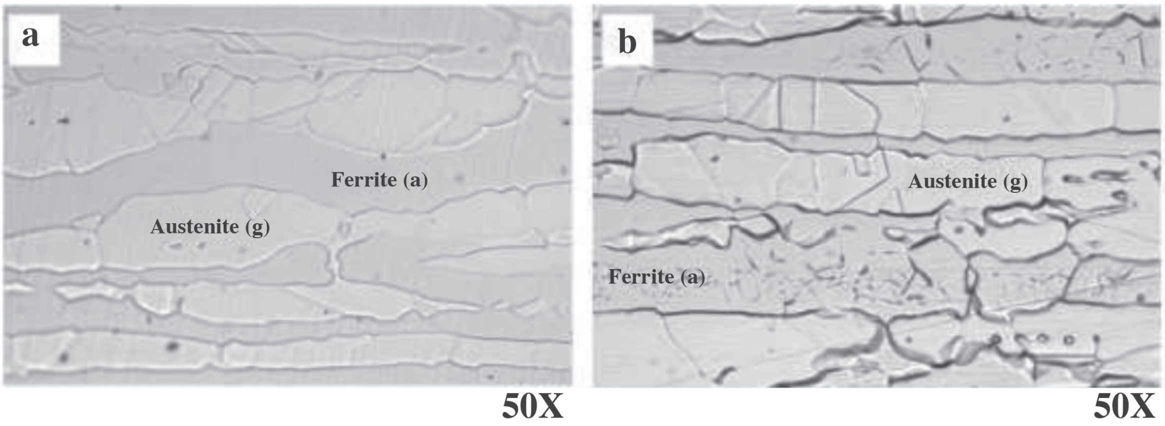

Fig. 3. Microstructure of super alloy in annealed condition; a) - Solution annealed with no plastic deformation, b) - 16% plastic strain. *10% Oxalic acid etching.*

The same etched surfaces were evaluated using scanning electron microscope. Deformation marks on ferrite (a) and austenite (g) grains can be seen clearly at higher magnification (Figs. 4a & b) of 16% plastic strain specimen. In the centre there is a cross-grid network of screw deformation bands. The Figure also illustrates that the deformation in ferrite has formed a well defined slip band structure. The features of the structures in the ferrite grains were similar to those reported in the literature (Chiu, 2006). Small voids coupled with the slip bands exist in austenite phase. Dislocations are also located and clustered near to the ferrite austenite interface as shown in Fig. 4b. Generally the more densely populated bands are within the grains that were more susceptible to deform.

Electrochemical Tests*:* The potentiodynamic results at 90ºC in 3.5% sodium chloride solution are shown in (Fig. 5). The results show the effect of metallurgical changes caused by plastic deformation on the pitting corrosion potential of super duplex stainless steels. Specimens had different corrosion resistance to the corrosive. The pitting corrosion resistance of the annealed (zero cold work) samples decreased after cold work (plastic deformation). The passivity region of the annealed samples is much wider than those with plastic deformation. The wider passivity range manifested the delay in pitting corrosion as indicated by pitting potential value. The difference in pitting corrosion values at two cold work levels is slight compared to the annealed condition samples.

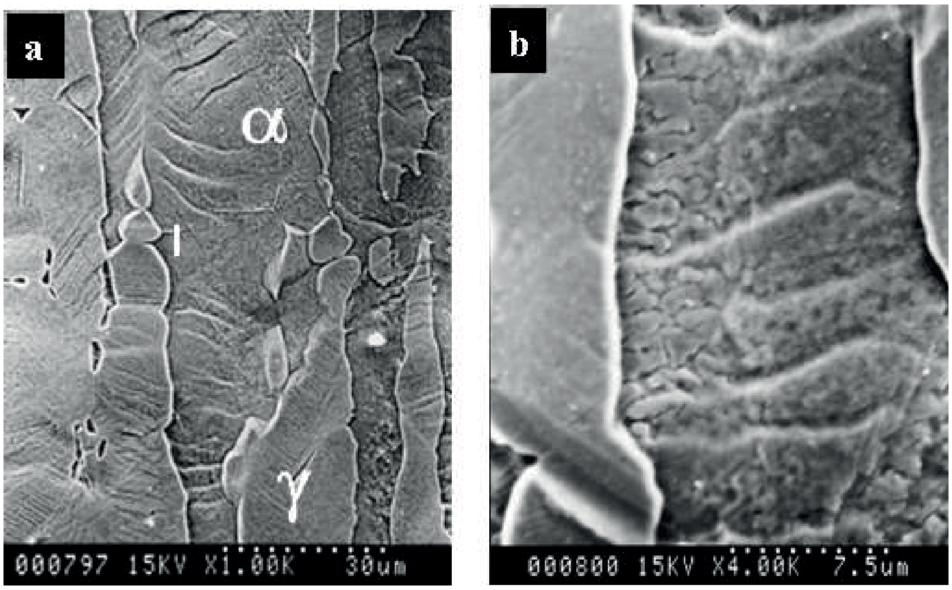

Fig. 4. SEM photographs; a) - 16% plastic strain, b) high magnification at local I. *10% Oxalic acid etching* .

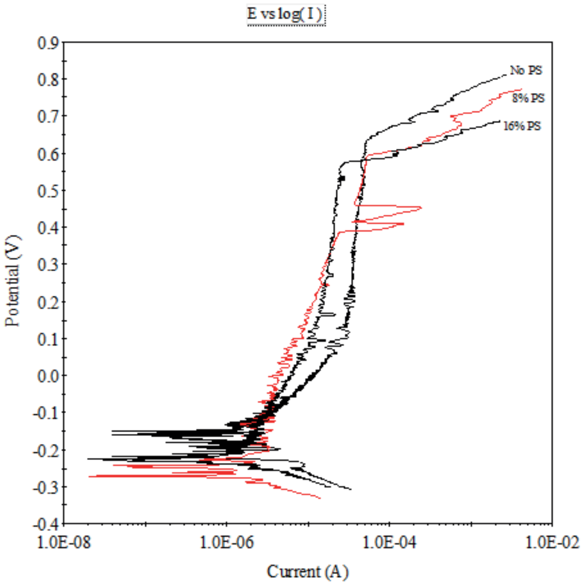

Fig. 5. Potentiodynamic polarization curves of super duplex alloy in 3.5% sodium chloride at 90ºC.

***Corrosion morphology**:* Corrosion morphology results showed that the plastic strain produced defects that acted as anodic sites for pitting corrosion initiation. The intense slip bands formed in the grains promoted rapid dissolution during the corrosion test. Figs. 6a-c) shows the corrosion morphology of 8% plastic strain specimen. The results illustrate an isolated shallow pit with edges indicating that the ferrite grains are the candidate propagation path as can be seen at higher magnification images in (Figs. 6b & c).

The morphology of corrosion was transformed to preferentially attack along the ferrite grains on 16% plastic strain specimen as illustrated in (Figs. 7a-c). Moreover, the fraction of cluster pits increased at grains containing shear bands or deformation marks. The presence of such clusters of attack specimen can be attributed to the sharp increase in shear bands on ferrite grains. Shear bands and deformation marks had poor corrosion resistance.

DISCUSSIONS

Plastic deformation resulted in a wide variety of slip bands in the deformed structure. Moderately and low intense slip bands were formed in the structure plastically deformed at 8% plastic strain. For specimens strained to 16% plastic strain, slip bands of higher intensity were produced. Intense slip bands were always produced in the ferrite grains and at austenite grain. This depends on the stacking fault energy of each phase. The value of stacking fault energy (SFE) plays an important role in the deformation process. Low SFE in nitrogen austenitic stainless steels promotes planar dislocation slip and twining, while a high concentration of nitrogen interstitials increases the friction stress against dislocation motion and twining nucleation (Jandova, 2004).

The deformation marks and dislocation structure in the straining course of the dual phase austenite-ferrite stainless steel are illustrated in the optical

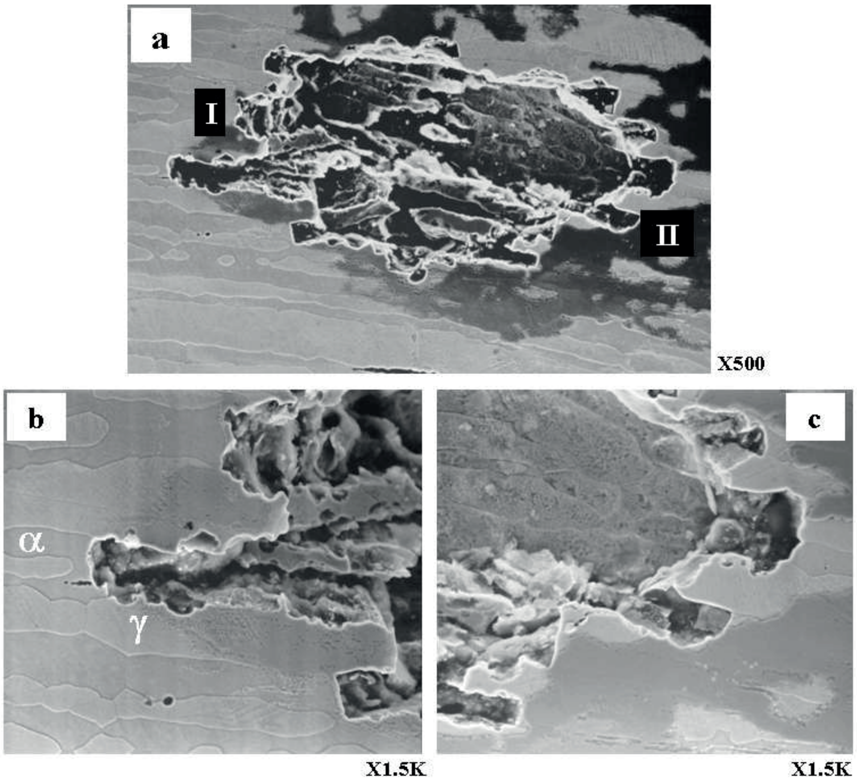

Fig. 6. Pitting corrosion attack on 8% plastic deformed super duplex alloy in 3.5% sodium chloride solution at 90ºC; a)- General view for a shallow pit , b and c)- Higher magnification at the pit propagation edges.

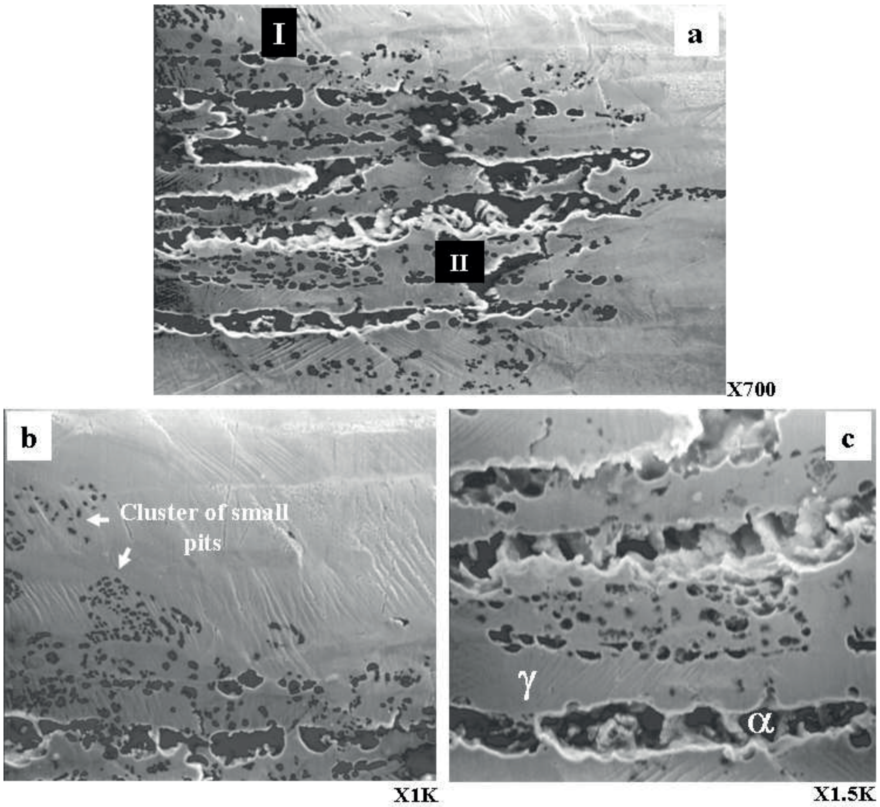

Fig. 7. Pitting corrosion attack on 16% plastic deformed super duplex alloy in 3.5% s sodium chloride solution at 90ºC; a)- General view for severe attack, b)- high magnification at circumferential pit side and at the deformation bands and c)- High magnification inside the pit along the grains.

and scanning electron microscope results in (Figs. 3 and 4a & b). The dislocation behavior at less plastic deformation is controlled and accommodated by the softer austenite phase. At high plastic strain the presence of slip bands is related to the plastic deformation of the two phases in the alloy especially ferrite. The ferrite phase accommodates more dislocation than the austenite phase at high plastic deformation. The high plastic deformation produces dislocation angles, which were more obvious in the ferrite phase. Deformation structure observed in the study are in good agreement with results found by (Mateo *et al* 1969) on the substructure evaluation after cyclic stress – strain tests on duplex alloy. After exposure to the corrosive environment, slip bands on ferrite grains were observed as nucleation and preferential sites for corrosion attack by chloride. As demonstrated previously that the strain-induced martensite and the residual stresses are significantly introduced on the surface, which affects the localized corrosion resistance by increasing the number of active anodic sites on the surface (Elayaperumal, 1972; Randak & Trautes, 1987). The susceptibility of cold worked 18 Cr – 10 Ni – 2 Mo steel to pitting corrosion in a NaCl solution was reported with the number of pits generally increasing with increase in the deformation, except in the 15 %deformation where low pit count and large average pit size were reported (Newman, 1987). In this study it was found that cold work of super duplex stainless steel to plastic strain values of 8% and 16% had an adverse effect on the corrosion resistance of the alloy in 3.5% sodium chloride solution. The results of this study further support the significant effect of plastic strain on the corrosion resistance of stainless steels. The results also indicate that the corrosion resistance of super duplex stainless steel was highly affected by the metallurgical structural changes caused by the plastic deformation. Dislocations and slip bands inside the microstructure work as corrosion initiation sites.

CONCLUSIONS

Straining in axial tension caused severe deformation of the passive film and the grains. The presence of deformation has a significant effect on the corrosion resistance of the super duplex stainless steel alloy. Corrosion resistance, as measured by pitting potential, was decreased by plastic deformation. Defects caused by deformation worked as anodic sites promoted corrosion dissolution rate. Deformation bands acted as acceleration preferential locations for new pits. Transformation to severe corrosion attack was along the most highly deformed grains which were mainly ferrite. Deformation on ferrite phase was more pronounced, This causing ferrite to be preferentially attacked by chloride.

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