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LOCALIZED CORROSION AND STRESS-CORROSION CRACKING BEHAVIOR OF
STAINLESS STEEL WELDMENTS

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I. PITTING BEHAVIOR OF DUPLEX 308 L STAINLESS STEEL
IN METHANOL/WATER/HCL

Abstract

I Localized Corrosion (Pitting) experiments have been conducted as a function of alloy microstructure (% δ ferrite) in acidified water/methanol solutions. It has been shown that the pitting resistance of duplex stainless steels is primarily a function of the δ/γ interface, relatively independent of the interfacial area or of the volume percent of the ferrite, in strongly passivating solution (those which contain significant amounts of water). These results suggest that the integrity of the passive film is affected by the chemical composition of the δ/γ interfaces. Specifically, this behavior is thought to be associated with segregation of sulfur to this interface. Thus the phase boundary acts as a two dimensional sulfide inclusion. (Three dimensional sulfide inclusions are the preferred sites for pit nucleation in single phase alloys). Reducing the water/methanol ratio in the solutions further increases localized corrosion susceptibility for all alloy microstructures examined. At a critical water concentration pit susceptibility is fixed independent of the ferrite content of the alloy. This suggests that the integrity of the passive film is reduced to the point where the "weak" film associated with phase boundaries (or inclusions) is no longer a preferred site for pit nucleation and general pitting is observed on the alloy surface.

I. INTRODUCTION

This study examines the effects of microstructure on the pitting behavior of type 308 L stainless steel. The original single phase austenitic structure was transformed to duplex austenitic-ferritic phases of varying ratio by iso-thermal heat treatment followed by quenching. Water-methanol mixtures containing 0.5 mol HCl/l were used as test solutions. The pitting behavior as a function of the δ -ferrite content of the alloy and of the water content of the solution was examined.

Although the initial process of localized breakdown of the passive film on stainless steels has been studied for years, this mechanism is not yet completely understood (1). Several mechanisms have been proposed, suggesting that pits form in one-phase steel alloys at the grain boundaries (2-5) or at the nonmetallic inclusions (6-10).

Sulfide inclusions are particularly susceptible. This is observed not only in austenitic (11-13) but also in ferritic (14,15) stainless steels. Several methods of investigation have shown that these susceptible inclusions are primarily manganese sulfides (12,14,16), or sulfides of the (Fe,Mn)S type (17).

Stainless steels with duplex structure show another mode of localized corrosion. The alloying elements which act as stabilizers of austenite, e.g. Ni, C, N, are partitioned to the austenite phase, whereas in the ferrite phase a partition of the elements stabilizing ferrite such as Cr and Mo occurs (18,19). In the pitting corrosion range this partitioning of solute elements leads to an increased susceptibility for pit formation at the phase boundaries. The beginning of the formation of pits at the ferrite-austenite phase boundaries was observed not only in the welded 304 (20) with very fine needle-shaped ferrite structure

but also in URANUS 50 (19) with a large proportion of continuous ferrite. In the active corrosion range an uneven distribution of alloying elements manifests itself in preferential dissolution of ferrite (22-24).

The influence of water on the corrosion behavior of materials that can be passivated is significant. In water-free alcohols containing hydrochloric acid, stainless steels 304 and 316 corrode actively. With increasing water content, above a critical water concentration, a transition to passivity is observed. With increasing water concentration the critical current density decreases and the passivation potential shifts to more active values; the current density in the passive range is reduced and the passive range itself is increased (21,22). It is particularly significant that the passivation potential depends only on the water concentration and not on the type of alcohol (23). Also, a direct influence of the water in the pitting corrosion range can be observed. With increasing water content the pitting potential is shifted to more noble values (24-26). For example, in methanol containing HCl, for the range 1-6% water, a linear increase of the pitting potential of chrome with water content of the solution was determined (24); in ethanol containing HCl the pitting potential of titanium exhibits a linear dependence on the logarithm of the water concentration in the range 4-6% H₂O (26).

II. EXPERIMENTAL

1. Materials

Stainless austenitic steel 308 L with the following chemical composition was used:

C	Cr	Ni	Si	Mn	P	S	Co	Mo	Cu
0.021	19.69	9.30	0.38	1.53	0.026	0.012	0.17	0.27	0.18

This material was supplied as commercial welding electrodes: round bars 35 cm long with a diameter of 5 mm. After removing the inorganic coating, the bars were roughly ground, then rolled to strips 1 mm thick and cut into small sheets 7 x 7 x 1 mm. The alloy was heat-treated in a vertical furnace, under flowing argon, for 3 hours at temperatures from 1275 - 1375°C. Figure 1 shows the pseudo binary phase diagram for the alloy, (27) including the two phase region, and figure 2 shows the volume % δ -ferrite content as a result of each heat treatment. The samples were quenched in saturated calcium chloride solution which was cooled to -20°C by mixing with dry ice. Prior to heat treatment the samples were held at 1015°C for 30 minutes and quenched in the same CaCl_2 solution to eliminate the quasi-martensite formed on rolling (~15). After heat treatment the sheets were polished on all sides with 600 grit paper and cleaned in acetone. It should be noted that the structure of the heat treated samples differs fundamentally from the structure of a welded steel of the same type. In contrast to the fine needle-like ferrite structure of welded steel (13,18), well-developed ferrite crystals are observed in the heat treated samples. These are larger with increasing ferrite content (determined by Mage Gage) and become continuous (fig. 3 and 4) as amounts of ferrite increase.

2. Test Solutions

Mixtures of water and methanol containing 0.5 mol HCl/l, used as test solutions, were prepared from deionized water, methanol and concentrated hydrochloric acid. The acid concentration was controlled by titration with KOH against phenolphthalein. Before each measurement, solutions were deaerated for one hour with prepurified argon with intensive stirring agitation. Specimens were supported on a simple

platinum wire platform with a three point contact with the specimen. In this way possible errors due to crevice corrosion effects are largely eliminated. Examination of the samples after the tests showed no crevice corrosion at the contact points, in accordance with other results (13,28). Potentiodynamic sweeps were conducted according to the following technique. The specimen was held at the corrosion potential for 10 minutes, followed by anodic polarization at 1000 mv/min, until the critical current density was passed and the measured current density was about half the critical current density. At this point polarization was continued at 2 mv/min until the passive current was reached, at which point the potential was held for a period of 10 minutes. The potential was then continuously increased at 2mV/min until the pitting potential was reached. Pitting potentials were defined as the potential above which no repassivation occurred, i.e. when a monotonic increase of the current was registered. Using this technique anodic ferrite dissolution in the active range was suppressed, and a more uniform passive layer on the metal surface was obtained, leading to a better reproducibility. For a few experiments to determine the critical current density, passivation potential and the passive current density a scan rate speed of 2mV/min was used throughout the polarization. All the measurements were carried out at room temperature. The reference electrode used was a saturated calomel electrode.

III. RESULTS AND DISCUSSION

1. Structural Parameters

Figures 5-12, show that the corrosion behavior of the steel is adversely influenced by the formation of δ -ferrite. The passivation potential is shifted towards positive values with a marked increase between 0 and 1 vol. % ferrite (Fig. 5a). The critical current density

for passivation also shows a large shift between 0-1% δ , followed by a further increase of the current values directly proportional to the increasing ferrite content (fig. 5b). Only one solution, 70 Vol. % water, is shown. Similar results are observed for other test solutions. Figure 6 shows that the passive potential and the critical current density are strongly affected by water concentration with a sharp rise in both values at $\sim 50\%$ H_2O . The examples shown are for a 5% ferrite alloy. An increase of the ferrite content also affects the pitting potential (fig. 7). A sharp decrease occurs between 0% and 1% ferrite in all the water contents (100-20 Vol. % H_2O). After this discontinuity the pitting potential values in corroding media with 100 and 70 Vol. % water decrease gradually. In corroding media with 50 and 20% water a further increase of the ferrite content has no further influence on the pitting potential. The marked decrease of the pitting potential values, from the higher pitting potential of single phase samples to the potential of the samples containing ferrite, indicates a change of the mechanism of pit formation. In order to understand the pitting potential results obtained, a series of pit initiation experiments were conducted by immersing specimens polished to 0.06 μm alumina in an 0.33 molar $FeCl_3$ solution for one minute. It was observed that pits initiated preferentially in samples with 0% ferrite at nonmetallic inclusions, in samples containing ferrite, however, pits initiated at the ferrite-austenite phase boundaries (Fig. 13, 15), independent of ferrite content. These results correspond with those of other investigations (19, 20). The nonmetallic inclusions, at which the pits initiate, are mainly manganese sulfide in accordance with previously published results (12, 14, 16, 17). After initiation the pits at the δ/γ phase boundaries propagate evenly into the austenite as well as into the ferrite phase.

It is difficult to say which phase is attacked more because several propagated pits were found not only on both sides of the phase boundary but occasionally in ferrite only or in austenite only. Fig.13 -15 also show that the pits can initiate at very small ferrite crystals. It may therefore be assumed that at sites where pits can be seen in the bulk austenite matrix, originally small ferrite crystals existed. Pit formation on the δ/γ phase boundaries, however, is not intrinsically due to the existence of a second phase with its resultant boundary, as shown by studies of another type of phase boundary (29,30). By cold working or by cooling to -196°C various quantities of martensite were generated. This second phase did not influence the pitting potential of the steels. Accordingly, the shifting of the pitting potential of samples containing δ -ferrite must depend on compositional variation between the phases. This different composition is caused by an uneven distribution of the alloying elements which occurred during the heat treatment. In the cold worked or quenched alloys practically no diffusion process occurs. With increasing ferrite content, the ferrite phase becomes slightly poorer in chrome and richer in nickel. For example, in a specimen with $\sim 5\%$ ferrite, the ferrite phase should contain approximately 23% Cr and 7% Ni; at $\sim 30\%$ ferrite this phase should contain $\sim 22\%$ Cr and 8% Ni. The austenite phase of these samples can be expected to contain $\sim 19\%$ Cr and 11% Ni vs. 18% Cr and 12% Ni. In order to determine these phase compositions, microprobe traces of the alloy were performed. As shown in fig. 3 and 4 these values correspond well with expected values. These results suggest that the nature of the passive film is significantly different in the vicinity of the phase boundary, and that the pitting behavior is not strictly a function of macro-compositional changes in δ vs. γ

phases. Rather, it is suggested that impurity segregation of sulfur, which has been recently reported by Stoker and Lumsdem (31), may be responsible for the pit nucleation sites. According to this model, sulfur, segregated to the δ/γ boundary, would play precisely the same role as sulfide inclusions in single phase alloys, creating a weak passive film over the boundary. Clearly a model of chromium depletion at the boundaries due to growth of the ferrite phase cannot explain the results.

2. Influence of the Water Contents.

A decrease of the water content of the acidified methanolic corroding media decreases the corrosion resistance of stainless steels. The passivation potential shifts to more noble values and the critical current density is decreased (fig.6a,b). The sudden increase of both these values below 50 Vol. % water suggests a change in the passivation mechanism in corroding media of high and low water content in agreement with other results (21,23).

The lower the water content, the more difficult it is to induce passivity. Below a critical water concentration no passivation occurs. Because the water molecules are necessary for the formation of passive layers, a similar effect can be expected also for the stabilization of passivity. With decreasing water concentration the integrity of the passive film decreases. For all specimens, the pitting potential shifts to more negative values (fig.8). However, for specimens with 0% ferrite the shift is greater than in the samples containing ferrite. Figure shows a schematic diagram of the pitting potentials as functions of ferrite and water content. Figure 10 shows the potential differences between the specimens with 0 Vol. % and 1 Vol. % δ -ferrite. A linear decrease of the potential differences with diminishing water content is indicated.

The extrapolation of the straight line shows that in low water contents these differences disappear. Below 10 Vol. % water no passivation occurs, and the pitting potential of the austenitic and duplex 308 L steel is of the same value at about 15 Vol. % water. Repassivating potentials are also decreased with decreasing water content (fig. 11 and 12). These results show that the range of the repassivating pitting in the austenitic samples is larger than in the samples containing ferrite, but that it diminishes more distinctly with decreasing water content. In 20 Vol. % H_2O the potential range of repassivated pits is ~ 60 mV. The dependence of the pitting potentials on the water content and particularly the steep decrease in the austenitic sample with decreasing water concentration can be explained as follows:

In an aqueous corroding solution the passive layer of all the samples is stabilized by a sufficient quantity of water molecules. The reaction of the metal surface with the water molecules can be described with the following equation (32).

In the austenitic sample the pits initiate mainly at inclusions (presumably manganese sulfides). In the samples containing ferrite the pits initiate mainly at the ferrite-austenite phase boundaries. A penetration of the passive film can thereby, in both cases, still easily be repassivated. With decreasing water content the integrity of the passive film decreases, and a nucleated pit is more difficult to repassivate due to the low amount of "free" water molecules. The surface reaction (32).

begins to prevail, forming soluble products. Accordingly, pit formation does not remain localized at inclusions or at the δ/γ phase boundaries, but can occur generally. The mechanism of pit formation accordingly become identical for all areas on the alloy surfaces.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 6

Fig. 7

Fig. 8

Fig. 13

Fig. 14

II STRESS CORROSION CRACKING OF 304 STAINLESS

STEEL IN CHLORIDE AND SULPHATE SOLUTIONS

ABSTRACT

Slow strain rate stress corrosion cracking studies have been performed on single phase and duplex stainless steels as functions of solution chemistry, temperature, and alloy heat treatment (sensitization). Results have been obtained which indicate that sulfate additions to chloride solutions inhibit transgranular or interphase SCC in the same manner in which sulfates inhibit pitting, independent of the solution temperature. Thus it is suggested that local breakdown of passive films is responsible for both pitting and SCC initiation and sulfates act to repair such films.

Additionally, it has been shown that the onset of SCC due to sensitization occurs rather suddenly. A transition from transgranular SCC to intergranular SCC and a concomitant shift in the critical cracking potential in deaerated solutions occurs over a 0.5 hr. increase in isothermal heat treatment at 620°C. Further experiments are being performed in order to determine if carbide precipitation in grain boundaries is observed over the same time scale.

STRESS CORROSION CRACKING OF 304 STAINLESS STEEL IN CHLORIDE AND SULPHATE SOLUTIONS

A large number of investigations have been carried out to understand the mechanisms of stress corrosion cracking in annealed and sensitized 304 stainless steel in high purity water at 290°C.

Excellent reviews of past work on stress corrosion cracking of iron and nickel base alloys are available (1-3). 304 stainless steel is an important structural material for water cooled nuclear reactor systems. Many incidents of stress corrosion cracking have been reported in these systems (4). It is therefore important to understand the processes involved.

Annealed 304 stainless steel usually cracks in a transgranular mode, whereas sensitized 304 stainless steel usually cracks in an intergranular mode. 304 stainless steel becomes sensitized (due to chromium carbide precipitation at grain boundaries) when heat treated within the temperature range 480-815°C, such as experienced during welding or stress relieving procedures.

A number of investigators studied stress corrosion cracking of 304 stainless steel in high purity water. For these investigations experiments at controlled potentials were performed by adding sodium sulphate (Na_2SO_4) to increase the electrical conductivity of the water (5,6). Sodium sulphate does not cause localized corrosion in austenitic stainless steel in high temperature water nor does it have any inhibiting or accelerating effect on general corrosion (5).

When chloride ions, as NaCl, were added to high purity water, the stress corrosion process was accelerated (7). The occurrence of stress corrosion

cracking was observed at potentials noble to a threshold cracking potential (7-12).

This potential was attained by one or both of the following methods:

- 1) Application of a potential noble to the threshold cracking potential.
- 2) Existence of sufficient dissolved oxygen to shift the potential into the specified region.

The threshold cracking potential and the pitting potential for annealed 304 stainless steel were found to be identical (7,11,13). Cracks were observed to be initiated from pits (7). In the presence of chloride ions Na_2SO_4 is known to have an inhibiting effect. Addition of 1% Na_2SO_4 to a boiling MgCl_2 (42%) solution delayed stress corrosion cracking of 304 stainless steel for 84 hours (14).

Two approaches to understanding the role of sulphates in inhibiting stress corrosion cracking of 304 stainless steel in chloride solutions have been considered:

- 1) An increase in the rate of repassivation due to sodium sulphate addition would slow the rate of crack propagation and therefore could improve the metal's resistance to stress corrosion. A similar phenomenon has been observed for NaNO_3 (15) in chloride solution.

- 2) Sulphate ions adsorb preferentially to chloride ions on the surface of the metal, as shown by Rosenfeld and Maximtschuck (16). They observed that more noble potentials increased the chloride adsorption on the surface and addition of sulphate to chloride solution resulted in a decrease in the amount of chloride ions adsorbed. This observation could explain the inhibiting effect of sulphate on the pitting corrosion of 304 stainless steel in chloride solution.

Experiments performed at room temperature demonstrate that addition of increasing amount of Na_2SO_4 to 0.1N NaCl solution shifted the pitting potential of 304 stainless steel to more noble potentials (17).

An identical shift of the threshold cracking potential is expected to occur, thus improving the metal's resistance to stress corrosion cracking.

The purpose of this study is to understand the mutual effects of sulphate and chloride ions in the initiation and propagation of stress corrosion cracks.

An understanding of these processes is necessary for successful use of inhibitor additions to prevent stress corrosion cracking of 304 stainless steel.

This program includes potential controlled constant extension rate stress corrosion experiments of 304 stainless steel. The experiments are conducted at a strain rate of $1.1 \times 10^{-5} \text{ s}^{-1}$. The tensile specimens are cut from a cold rolled sheet, and the rolling direction is parallel to the length of the specimen. An Ag/AgCl electrode is used as a reference electrode.

The solution is deaerated high purity water with a resistivity greater than 15 megaohm-cm, to which chloride and sulphate ions as NaCl and Na_2SO_4 are added, respectively.

The solution is pumped at a flow rate of 2 liters per hour and the system's pressure is kept by a back pressure regulator.

Variables under investigation are:

A) Heat treatment of 304 stainless steel.

- 1) Solution Anneal - 1038° in argon environment, followed by water quenching.
- 2) Heavy sensitization - solution anneal (as in 1), followed by heat treatment at 620°C for 24 hours in argon environment, and then air cooling.

3) Mild sensitization - solution anneal (as in 1), followed by heat treatment at 620°C for 1/2 hour in argon environment and then air cooling.

B) Temperature $\sim$ 80°C - 288°C.

C) $\text{Cl}^-/\text{SO}_4^{=}$ concentration.

D) Applied potential.

Results from this study will enable a correlation of threshold cracking potential data with pitting potential data.

Specimens are examined by scanning electron microscopy to determine the fracture mode. Energy dispersive X-ray analysis is being used to determine the elements on the fractured surface.

Auger analysis has been used to determine the existence of chloride and sulphate ions in the passive film and their relative amounts in the passive film.

PRELIMINARY RESULTS

Experiments were performed at 288°C in a deaerated solution. It was shown that increasing the amount of sulphate ions in 100 ppm NaCl solution (Fig. 1) shifted the critical threshold cracking potential of annealed 304 stainless steel to more noble potentials; thus extending the range of potentials where the metal is immune to stress corrosion cracking.

Reduction of the chloride concentration in a sulphate solution (Fig.2) shifted the threshold cracking potential of annealed 304 stainless steel to more noble potentials, and a reduction to 1.8 ppm Cl^- caused the specimen to fail in a ductile mode even at an applied potential of +700mv (vs. Ag/AgCl electrode).

Decreasing the chloride concentration did not change the threshold cracking potential (Fig. 3). Therefore, the initiation of stress corrosion cracking in sensitized 304 stainless steel was independent of the chloride concentration, indicating that this phenomenon could not be explained by a model based on adsorption. On the other hand, the chlorides played an important role in accelerating the propagation of cracks, and higher chloride concentrations caused the specimen to fail at lower stresses and in a shorter period of time.

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EFFECT OF SULPHATE ON SCC OF ANNEALED 304 SS IN 100 PPM Cl

FIG NO. 2

EFFECT OF Cl^- IONS ON SCC OF ANNEALED 304 SS IN 100 PPM $\text{SO}_4^{=}$

FIG 10.3
EFFECT OF Cl^-

IONS ON SCC OF SENSITIZED 304 SS IN 100 PPM SO_4

PERSONNEL DATA

Currently Assigned to Program

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Publications resulting from research performed under DOE Contract #DE-AS02-76ERO2462

1. Previously Reported.

"Slow Strain Rate SCC of Type 304 Stainless Steels" Corrosion 33, 67 (1977), F. Stalder and D. J. Duquette.

"Stress Corrosion Cracking in Duplex Stainless Steel Weldments," Welding Journal, 57(6) 1978, p. 175, W. A. Baeslack III, W. F. Savage and D. J. Duquette.

"STEM Microanalysis of Duplex Stainless Steel Weld Metal," Scanning Electron Microscopy, I, 213 (1978), C. E. Lyman, P. E. Manning, D. J. Duquette and E. Hall.

"The Effect of Test Method and Surface Condition in Pitting Potential of Single and Duplex Phase 304L Stainless Steel," Corrosion, 35, 151 (1979), P. Manning, D. J. Duquette and W. F. Savage.

"Slow Strain Rate Stress Corrosion Testing at Elevated Temperatures and High Pressures," to be published Corrosion Science, 1980, P. Andresen and D. J. Duquette.

"Effect of Nitrogen on the Microstructure and Stress Corrosion Cracking of Stainless Steel Weld Metals," Welding Journal, 58(3), 835, (1979), W. A. Baeslack III, W. F. Savage and D. J. Duquette.

"The Effect of Strain Rate on SCC in Duplex Type 304 Stainless Steel Weld Metal," Met. Trans., 10A, 1429 (1979), W. A. Baeslack III, W. F. Savage and D. J. Duquette.

"Sulfur and Phosphorus Segregation in Duplex Stainless Steel Weld Metal", Microbeam Analysis Ed. D. Newbury, p. 135, (1979), C. E. Lyman.

2. Publications for 1980-81

"The Effect of Temperature (25°C-290°C) on Pit Initiation In Single Phase and Duplex 304L Stainless Steels in 100 ppm Cl⁻ Solution," Corrosion Science, 20, 587, (1980), P. E. Manning and D. J. Duquette.

"The Effect of Retained Ferrite on Localized Corrosion in Duplex 304L Stainless Steel," Research Supplement 59(9), p. 2605, (1980), Welding Journal, P. E. Manning, D. J. Duquette and W. F. Savage.

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"Effect of Chloride-Ion Concentration and Applied Potential on the SCL Behavior of Type 304 Stainless Steel in Deaerated High Temperature Water," Corrosion, 36, 85 (1980), P. A. Andresen and D. J. Duquette.

"The Effects of Dissolved Oxygen, Chloride Ion and Applied Potential on the SCL Behavior of Type 304 Stainless Steel in 290°C Water," Corrosion, 36, 406, (1980), P. A. Andresen and D. J. Duquette.

"Slow Strain Rate Stress Corrosion Testing at Elevated Temperatures and High Pressures" Corrosion Science, 20, 211 (1980), P. Andresen and D. J. Duquette.

"A STEM Examination of the Localized Corrosion Behavior of a Duplex Stainless Steel" Corrosion, 36, 246 (1980), P. E. Manning and D. J. Duquette.