LOCALIZED CORROSION AND STRESS CORROSION CRACKING BEHAVIOR OF
AUSTENITIC STAINLESS STEEL WELDMENTS CONTAINING
RETAINED FERRITE

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MASTER

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ABSTRACT

Localized corrosion and stress corrosion cracking experiments have been performed on single phase 304 stainless steel alloys and autogeneous weldments containing retained delta ferrite as a second phase. The results of the pitting experiments show that the presence of delta ferrite decreases localized corrosion resistance with pits initiating preferentially at delta ferrite-gamma austenite interphase boundaries. This increased susceptibility is reversible with elevated temperature heat treatments which revert the metastable ferrite phase to the equilibrium austenite phase. Experiments have also been conducted as functions of surface preparation, pH, Cl^- concentration and temperature from 20°C to 290°C. These experiments indicate that pitting tendency for both single phase and two phase alloys is controlled by the physical properties of the passive films which are naturally formed.

The results of the SCC experiments have shown that, for two phase alloys at temperatures from 20°C to 290°C, the ferrite phase also significantly affects stress corrosion resistance. At low temperatures and low pH the ferrite phase is preferentially dissolved, while at intermediate temperatures and pH's the δ/γ interface is the preferred crack path. At high temperatures cracking is associated with pitting, and depends sensitively on O_2 concentration of the environment.

TECHNICAL PROGRESS REPORT

Localized Corrosion

Experiments on localized corrosion (pitting) in single phase and duplex phase 304L stainless steels have been performed using potentiostatic, potentiodynamic and scratch test methods. Variables which have been examined include surface conditions, heat treatment, chloride ion concentration, pH and temperature.

It was found that single phase alloy pitting potentials were a strong function of the surface condition and the test method used while the duplex phase alloy pitting potentials were independent of them. This is explained by the nature of the pit initiation sites, which are the sulfide inclusions in the case of the single phase alloy, and the residual delta ferrite/austenite interface in the duplex phase alloy.⁽¹⁾

In the single phase alloy, the length of sulfide/metal interface per unit area of microstructure was related to pit susceptibility and was used to explain the effect of surface condition on pitting potential. Additionally, the effects of heat treatment demonstrate the importance of the morphology of sulfide inclusions that are exposed to the electrolyte. The sulfide dissolution kinetics, which were found to control the pit initiation process, are influenced by the morphology of the inclusions exposed to the electrolyte, the time constraints of the various pitting corrosion test methods, the temperature and composition of the bulk electrolyte, and the spectrum of sulfide inclusion compositions present in the alloy.

In the duplex phase alloy, the sulfide inclusions do not play a role in the pit initiation process. Therefore, there is no effect of surface condition or test method. Since pitting occurs on the delta ferrite/austenite interface, the sulfide morphology and dissolution kinetics are not a factor

in pit initiation. Microanalysis results, which were obtained with Scanning Transmission Electron Microscopy, virtually disprove the chromium depletion theory for pit initiation at delta ferrite/austenite interfaces. The most likely explanation is a segregation of sulfur to the interface during the nonequilibrium solidification process associated with weldments.

The effect of temperature on the pit initiation in single and duplex phase alloys was investigated by the use of several passive film property tests that were conducted after film preformation at a temperature in the range of 25 - 289°C. Additionally, static and straining electrode pitting tests and Scanning Electron Microscopy pit initiation studies were performed.⁽²⁾ The properties measured as a function of temperature were the quality of the film (thickness and/or flaw density), the nature of the conductivity of the semiconductor oxide film, the static electrode pitting potentials, and the straining electrode pitting potentials. Results indicate that the transport of chloride ions through the film at temperatures above 220°C is a fast step; therefore, pit initiation is reaction controlled. At temperatures below 220°C, the results indicate that transport of chloride ions through the film at the sites most susceptible to pitting play a vital role in the pit initiation process and transport or mixed mode control occurs.

To summarize the major results of the localized corrosion program:

1. Sulfide dissolution kinetics were found to control pit initiation of single phase 304L stainless steel. The kinetics were influenced by the following variables: the method of conducting the pit initiation test, the morphology of the sulfide inclusions exposed to the electrolyte, and the composition and temperature of the bulk electrolyte.

2. Duplex phase 304L stainless steel, which solidified by a primary delta ferrite solidification mechanism, did not pit at metal/sulfide interfaces. The most susceptible site for pit initiation was the retained delta ferrite/austenite interface.

3. STEM composition profiles of Cr and Ni across the retained delta ferrite/austenite interface virtually disprove the chromium depletion theory for pit initiation at the interface.

4. The results of several film preformation tests, straining and static electrode pitting tests, and pit initiation studies indicate reaction control of pit initiation at temperatures greater than 220°C for static electrodes and a transport or mixed mode control of pit initiation at temperatures below 220°C.

5. Dissolution begins at sulfide/metal interfaces when chloride ions are present and a potential is applied at which sulfide inclusions of a particularly susceptible composition are thermodynamically unstable. Acidification of the local electrolyte as well as concentration of chloride ions occurs by migration. If geometrical conditions favor pit propagation, dissolution of the metal around the sulfide inclusion continues; if not, the pit repassivates. Initiation and repassivation events normally occur many times in pit embryos before pit propagation occurs.

6. The most likely mechanism for pit initiation at these interfaces is a sulfur impurity concentration on the interface that occurs from non-equilibrium solidification segregation and increases the dissolution tendency of the passive film over the interface. The sulfur impurity also inhibits repassivation kinetics at the delta ferrite/austenite interface.

7. The deviations in single and duplex phase alloy pitting potentials are caused by differences in the passive film composition and breakdown characteristics of the two different sites in these materials most susceptible to pit initiation. The response of the different passive films over these sites to changing environmental conditions, accounts for the deviation in single and duplex phase alloy pitting potentials.

8. As film preformation temperature increases, the quality of the film (film thickness and/or flaw density) increases and there is a tendency toward n-type conductivity in the semiconductor oxide film.

9. The pitting potential becomes more active as the temperature increases.

10. The morphology of sulfide inclusions, particularly the length of sulfide/metal interface per unit area of microstructure (L_{Me}/S), was found to influence the susceptibility to pit initiation on specimen edges to the electrolyte and on surfaces prepared by mechanical or chemical methods with varying roughness.

11. In cases where sulfide inclusion compositions change, such as high temperature (1300°C) heat treatment, other heats of 304L alloy, or other 300 series stainless steels, the L_{Me}/S value is not the primary factor in determining pit initiation resistance. The sulfide and matrix compositions are the critical factors that determine the pit initiation resistance.

12. The composition of the bulk electrolyte influences the ability to transport chloride ions through the passive film over the most susceptible pit initiation sites. Chloride ions are a necessary reactant in the complex sequence of reactions that result in pit propagation. Additionally, at high pH values competitive absorption of hydroxyl and chloride ions changes the pitting potential of the alloy in the noble direction.

13. The temperature of the bulk electrolyte influences the transport of chloride ions through the film, the absorption of chloride ions on the metal surface, and ensuing complex reactions that result in pit propagation.

14. When acidification from pH 4 to pH 2 of the various NaCl concentration solutions at several temperatures occurs, the nature of the sulfide dissolution kinetics and the time constraint from the potentiodynamic test explain the pitting potential data. The less aggressive solutions do not show enhanced pit initiation since the incubation time for sulfide dissolution is not exceeded by the time constraint from the potentiodynamic test. The highly

aggressive solutions (90°C) did not show enhanced pit initiation since the electrolyte at pH 4 is extremely aggressive and allow sulfide dissolution at very active potentials. The increased acidification to pH 2 provides very little increase in the already rapid sulfide dissolution kinetics. In electrolytes at 50°C and 0.5 or 1.0N NaCl concentrations the solution is sufficiently aggressive to reduce the incubation time for sulfide dissolution to an extent where reduction of the pitting potential occurs as measured by a potentiodynamic test.

15. The method of conducting the pit initiation tests was found to influence the time available for sulfide dissolution to occur at a given applied potential.

16. When sulfide dissolution kinetics did not control the pit initiation process, there was little effect of test method on the pitting potential, no difference in pitting potential between exposed and prepassivated specimen edges, and no effect of surface roughness on the pitting potential.

Stress Corrosion Cracking

The results of stress corrosion cracking of duplex weldments and weld affected zone as functions of chloride concentration and temperature to 154°C was relatively completely summarized in the 1978 technical progress report and are detailed in the attached reprint/preprints.⁽³⁻⁶⁾ Basically these results showed that cracking can occur in some cases by preferential ferrite dissolution and in other cases along γ/δ interfaces depending on the pH and temperature of the environment. Low solution temperatures and high extension rates promote intergranular cracking. It was also shown that continuous ferrite structures are more susceptible to SCC than are discontinuous structures in 1N HCl. Additionally there was a suggestion that some H_2 embrittlement of the ferrite might be occurring concurrently with transgranular cracking in the austenite. To test this hypothesis, cathodic charging of duplex weldments was performed in H_2SO_4 and in HCl solution with a variable amount of ferrite ranging from 6% to 23%. Wholly austenitic 304SS showed no appreciable effect of cathodic charging, however, ferrite containing weldments showed a considerable decrease in ductility when charged with hydrogen. It was also noted that fracture surfaces were altered from a dimpled, ductile rupture mode, to a quasi-cleavage appearance. The

reduction in ductility was shown to be a strong function of ferrite content, with the 23% ferrite (continuous ferrite) showing considerably less ductility than 6% ferrite. Thus, in addition to stress corrosion cracking under anodic conditions, duplex ferrite containing weldments show considerable susceptibility to hydrogen embrittlement.

In addition to experiments conducted at and near room temperature, CER (constant extension rate) SCC tests have been performed at 290°C in an instrumented autoclave. These results show that the critical component is high temperature, high pressure environments in dissolved O_2 . This fact has been known for a considerable period of time, however our experiments have closely related the effect of O_2 to pitting potentials when Cl^- is present in the environment.⁽⁷⁾ In deaerated solutions the onset of SCC (as measured by reduction in ductility) corresponds to the dynamic pitting potential of the alloy as a function of Cl^- concentration. We have also shown that the pitting potential for a straining electrode is more active than that of static electrodes, presumable because of mechanical film rupture. These results, coupled with analysis of reaction products and indicate that absorption of Cl^- may be a critical step in SCC of these alloys.

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