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

ANNUAL PROGRESS REPORT

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ABSTRACT

Localized corrosion (pitting) experiments have been performed on single-phase austenitic 304 stainless steels and on duplex 304 steels containing 6-8% retained δ ferrite as a result of rapid solidification (welding). Experimental variables included thermomechanical treatment, solution pH, chloride concentration and solution temperature.

It was shown that the pitting behavior of single-phase alloys is insensitive to heat treatment. For duplex steels, however, increasing time at temperature or higher temperature heat treatments resulted in resolution of metastable ferrite and pitting resistance improved with decreasing amounts of ferrite. Solution chloride concentration reduced pitting resistance in both single-phase and duplex alloys and the results of these experiments support a model for pit initiation which is consistent with Cl^- ion adsorption at the alloy surface, independent of the nature of pit initiation sites (inclusions for single phase and γ - δ interfaces for duplex steels). These results are consistent in the temperature range 22°C to 90°C although the absolute value of chloride pitting sensitivity changes with temperature.

Pitting experiments have also been conducted at 290°C in a flowing solution autoclave for single-phase materials with pit initiation occurring at ~ 100 mV vs. AgAgCl in 100 ppm Cl^- solutions.

Slow extension rate stress corrosion cracking experiments have also been conducted on single-phase and duplex steels in HCl at R.T., MgCl_2 at 154°C and in 0-1000 ppm Cl^- solutions at 290°C. In most cases the duplex steels are inferior to base metal and the δ - γ interfaces are the preferred crack initiation and early propagation sites. In some cases, the ferrite

phase is preferentially attacked while in other cases only the interfaces take part in the reaction. The distribution of retained δ ferrite is an important variable for cracking resistance in the duplex alloys. Continuous ferrite distributions are the most susceptible structures while either discontinuous ferrite distribution or blocky ferrite distributions are less susceptible. Thus ferrite distribution and not ferrite content is the more important variable for resistance. In autoclave tests, O_2 content of the solution was found to be the most significant environmental variable for resistance to stress corrosion cracking. For example, Cl^- concentrations of 0-1000 ppm show no effect on stress corrosion cracking resistance. With 2 ppm O_2 dissolved in the solution, however, increasing Cl^- concentrations result in significant decreases in stress corrosion cracking resistance. Potentials noble to the measured pitting potential also result in decreased stress corrosion cracking resistance even in the absence of O_2 . Fracture morphologies of specimens cracked at 290°C are similar to those observed for lower temperature failures.

TECHNICAL PROGRESS REPORT

A. Localized Corrosion

The major results of the localized corrosion studies are contained in the attached preprints. In addition to these results, a number of other experiments have been performed to examine the localized corrosion behavior of welded duplex stainless steels. Variables examined include heat treatment, environment pH, Cl^- concentration and temperature.

1. Effects of Heat Treatment

Fully austenitic (base metal) specimens were potentiodynamically polarized in 1N NaCl solution of pH 4 in a variety of thermomechanical treatments, i.e. cold worked 10%, annealed at 1050°C for 5 min. and at 1300°C for 8 hrs. and quenched. The latter heat treatment results in spheroidization of nonmetallic inclusions. Results of these tests showed no effect of thermomechanical treatments on pitting behavior. The critical pitting potential was unchanged and pit initiation invariably occurred at inclusion/matrix interfaces, independent of inclusion shape.

Weld metal containing nominally 6% δ ferrite retained from the welding process, showed a significant sensitivity to heat treatment. For example, as-welded steels show a 100 mV shift in pitting potential in the active direction, i.e. are more sensitive to pitting. Heat treatment at 1050°C for only a few minutes results in a shift of the pitting potential in the noble direction. For example, a five-minute heat treatment, which lowers the retained δ ferrite to 2-3%, results in a significant shift in pitting potential in the noble direction, while a one-hour anneal ($\sim$ 1% δ ferrite) shows a pitting potential which is within 20 mV of the potential observed for base metal and a 7-day anneal ($\sim$ 0% ferrite) shows a pitting potential which is equal to that

observed for the base metal. Thus, annealing of weldments to eliminate the retained second phase results in a significant improvement in pitting resistance.

2. Effects of Solution Chemistry

Pitting potentials of single-phase stainless steels have been reported to exhibit a linear relationship with Cl^- concentration; potentials becoming more active (less resistance to pitting) with increasing Cl^- concentrations. A similar relationship has been established for steels containing 6% retained δ ferrite (weldments) and the slopes of the ϕ_p vs. C_{Cl^-} are virtually identical for the two structures at room temperature. The ϕ_p (crit) relationship for single phase steels has been previously reported to obey an equation of the form:

$$-m \log(\text{Cl}^-) + b$$

where (Cl^-) is equal to the activity of the chloride ion. Results generated in this program show a slope (m) of -120 V per decade, with parallel slopes observed for both structures (22°C). At 50°C this slope increases to ~ -200 mV/decade for base metal and ~ -140 mV/decade for the two-phase structure, and at 90°C the slopes decrease to -170 mV/decade and -155 mV/decade, respectively. While these slopes disagree numerically with some previously reported data for 18-8 stainless steels, they are in qualitative agreement with the adsorption isotherm equation: amount adsorbed = $k_1 (\text{Cl}^-)^{1/n_1}$. Thus, the data support a pit initiation process which is driven by adsorption of Cl^- from the solution, independent of structural characteristics. On the other hand, the spread in actual pitting potentials is a function of pit initiation sites, with the duplex steels exhibiting pit initiation at δ - γ interfaces and the single-phase steels at sulfide inclusions.

In addition to pitting experiments in bulk samples, some experiments were performed on thin foils of the duplex steels for subsequent examination

by transmission electron microscopy. These foils were pitted by anodically polarizing the foils to the critical pitting potential and holding that potential for a short period of time. Subsequent TEM of the foils indicated that small pits, $\sim 500\text{-}800\text{ \AA}$ in diameter were initiated, with 95% of the pits located exactly at $\delta\text{-}\gamma$ interfaces. A few pits were also associated with the γ base metal. These data, in conjunction with STEM observations (see attached preprint) indicate that the intrinsic energy of the $\delta\text{-}\gamma$ interface is responsible for the decreased resistance to pitting of the duplex alloy. This is in contrast to previous suggestions that compositional gradients at or near the $\delta\text{-}\gamma$ interfaces could be responsible for decreased pit resistance.

Solution pH effects are currently being studied from pH 2 to pH 12. Preliminary results indicate that pH effects are a function of Cl^- concentrations. Additionally, there is a still unexplained anomaly at 50°C for very low pH's and high Cl^- concentrations with the single-phase material showing inferior resistance to pitting when compared with duplex steels. At RT and 90°C , duplex steels show inferior pitting resistance. At the present time, these results appear to be associated with the kinetics of dissolution near sulfide particles and this phenomenon will be investigated as part of our continuing program.

Preliminary experiments at 290°C have also been performed in a recirculating autoclave system in high purity water containing 100 ppm Cl^- with $<1\text{ ppb O}_2$. These results indicate a critical pitting potential of $-85 \pm 19\text{ mV}$ vs. Ag/AgCl (at temperature) for base metal samples. This portion of the program will be a major thrust for future research.

B. Stress Corrosion Cracking

Many of the results obtained in the SCC portion of this program are detailed in the attached preprints. In addition to those results, the following

observations are research in progress which will be prepared for publication when appropriate.

1. SCC in Type 304 and Type 304L Welded and Base Materials

- a. Room temperature cracking of duplex Type 304 and 304L weld metals under constant-extension-rate (CER) conditions occurs as a combination of stress-assisted ferrite dissolution and transgranular SCC in the austenite. Cracking under identical test conditions in wholly-austenitic Type 304 and 304L base metals occurs in a transgranular mode, with considerable crack branching and subsurface crack dissolution.
 - i. Type 304 base metal is more resistant to SCC in 1N HCl than Type 304 weld metal.
 - ii. Ferrite dissolution also occurs in unstressed specimens. However, a comparison of stressed and unstressed specimens indicates that ferrite dissolution under CER conditions is a stress-assisted process.
- b. SCC of duplex Type 304 and 304L weld metals under CER conditions in boiling MgCl_2 solutions occurs predominantly in an interphase mode. Combined interphase-transgranular cracking morphologies can also be observed at low extension rates and a high solution temperature (154°C). Cracking under identical test conditions in wholly-austenitic Type 304 and 304L base metals occurs in a combined transgranular-intergranular mode. Low solution temperature (135°C) and high extension rates promote intergranular base metal cracking.
 - i. The SCC susceptibility of Type 304 and 304L weld metals

is nearly the same as that of Type 304 and 304L base metals over a wide range of extension rates.

- ii. SEM fractographic studies have found that crack tip acidification may result in ferrite dissolution. SEM/EDS studies have shown that large quantities of ferrite remain on the fracture surface, indicating that cracking is an interphase process (probably related to the boundary dislocation structure) and that ferrite dissolution is an aftereffect of the cracking process.

2. Effects of Ferrite Content and Distribution on SCC in the Weldment Composite Region

- a. Room-temperature cracking of duplex weld metals tested under CER conditions in 1N HCl occurs as a combination of stress-assisted ferrite dissolution and transgranular SCC in the austenite. The most susceptible structure appears to be that which exhibits a continuous, vermicular ferrite microstructure.
 - i. Weld metals which exhibit discontinuous ferrite morphologies exhibit greater resistance because an increased amount of transgranular cracking is required for crack propagation.
 - ii. High-ferrite structures, which exhibit blocky ferrite and acicular austenite, also show a greater resistance to SCC.
- b. The SCC morphology and susceptibility of Type 304 + Nitrogen weld metals under CER conditions in boiling MgCl_2 at 154°C are dependent on several interrelated factors, including: nitrogen content, ferrite content, and ferrite morphology.
 - i. SCC in duplex Type 304 + N weld metals occurs in a combined

interphase-transgranular mode, with the interphase being preferred. SCC susceptibilities of these low Ferrite Number materials are very similar.

- ii. SCC in wholly-austenitic Type 304 + N weldments occurs in a combined intergranular-transgranular mode. The susceptibility of this structure is observably greater than that of duplex Type 304 + N weld metals.

3. Stress-Corrosion Cracking in the "Apparent" Weld Heat-Affected Zone

- a. The duplex unmixed zone of heterogeneous weldments on Type 304L stainless steel appears to be particularly susceptible to attack under CER conditions in room-temperature, low-pH solutions. Attack occurs as a combination of stress-assisted ferrite dissolution and TG cracking in the austenite.
 - i. Transgranular cracking in the austenite appears to occur by a tunneling mechanism similar to that observed by Scully and Harston.
 - ii. The simultaneous occurrence of ferrite dissolution and transgranular cracking in the austenite indicates that SCC of austenite in room-temperature solutions may occur by a mechanism other than film rupture (e.g., anodic dissolution of a strain-induced phase, or hydrogen embrittlement).
- b. The "apparent" weld heat-affected zone of heterogeneous weldments on Type 304L stainless steel base metal appears to be more resistant to SCC than the unaffected base metal in boiling MgCl_2 solutions under CER conditions.

- i. Failure of high ferrite and zero ferrite level weldments occurs in the unaffected base metal remote from the weldment composite region.
 - ii. Failure in autogenous Type 304L weldments occurs in the composite region, probably because of the lower strength of this region as compared to the unaffected base metal.
4. Crack Propagation Rate Determination Using Fracture Mechanics Techniques
 - a. Monitoring of room-temperature stress-corrosion crack propagation rates in contoured and bat-wing type constant K fracture mechanics specimens of Type 304 base and weld metals is unfeasible.
 - i. K_{ISCC} for Type 304 base material in 1N HCl is too high to allow single-crack propagation under plane strain conditions.
 - ii. Increasing the applied stress intensity (plane stress conditions) results in multiple crack initiation, extensive crack branching, and finally, gross specimen deformation.
 - iii. Applying anodic potentials to the specimen during testing considerably increases general corrosion on the specimen surface and does not appreciably influence stress-corrosion cracking.
 - iv. The general corrosion of ferrite in room-temperature test solutions makes the study of long-term crack growth measurements in duplex weld metals impossible.

5. High Pressure Autoclave Experiments

Stress corrosion cracking experiments have also been conducted at 290°C in an instrumented flowing solution autoclave system. These experiments were conducted on 304 stainless steels in the as-received condition, annealed (1080°C, 1 hour) and on single pass weldments containing -6% retained δ ferrite. Environmental variables which were examined included Cl^- concentration,

O₂ concentration and potential. All experiments were conducted using a slow extension rate ($1.1 \times 10^{-6} \text{ sec}^{-1}$) and comparisons were made on the basis of ductility losses as well as loss of maximum load sustained during a particular test when compared with a base-line test.

This base-line test was essentially one performed at temperature in high purity, high conductivity water (20 M Ω). The results of preliminary experiments indicate that, for all materials, the O₂ concentration of the solution is critical to SCC. For example, in the absence of O₂ (<1 ppb) no loss of ductility was observed from 0 ppm Cl⁻ to 1000 ppm for either as-received or weld metal samples. In 100 ppm Cl⁻ solutions, increasing O₂ concentration to 2 ppm resulted in a loss of ductility of 64-66% when compared with <1 ppb O₂ concentrations. The effects of chloride concentrations were also examined in O₂ saturated solutions, and it was observed that there was only a small effect of increasing Cl⁻ concentration to 1 ppm (11% loss in reduction of area) and a very large effect of further increasing Cl⁻ concentration to 10 ppm (62% loss in RA). One hundred ppm Cl⁻ solutions showed a still greater loss in RA of 77%. Actual reduction in cross sectional area was 58% at 0 ppm Cl⁻ and only 13% in 100 ppm Cl⁻.

The effect of electrochemical potential was also examined by instrumenting the autoclave with a counter electrode and a Ag/AgCl reference electrode. It was noted that, for the annealed steels in solutions containing 100 ppm Cl⁻ and <1 ppb O₂ (no loss of ductility), that anodic potentials from the corrosion potential (-700 mV vs. AgAgCl) to -200 mV vs. AgAgCl showed no effect on ductility. At -100 mV vs. AgAgCl (pitting potential) a decrease in ductility of 68% was observed. The reduction in ductility decreased to 40% at +200 mV vs. AgAgCl and showed a further increase at higher potentials, to -90% (5% R.A.) at +500 mV vs. AgAgCl. These data are shown in Table I. Because of the time

required for each of these experiments, the data trend from -100 mV to +200 mV vs. AgAgCl may be related to scatter, however, further experiments should establish the significance or lack of significance of the trend. It can be unequivocally stated, however, that anodic potentials above -100 mV vs. AgAgCl greatly reduce the ductility of annealed 304 stainless steels at 290°C.

Welded specimens show generally the same effects of applied potentials with ductility reductions of -54% to 92% being observed (Table II). Interestingly, a ductility minimum is observed at +100 mV vs. AgAgCl and the data appear to be a mirror image of the data observed for annealed steels. The significance of this observation is not well understood at this time.

Metallographic and fractographic observations of SCC failures have been performed by light microscopy and SEM. When SCC occurs, annealed steels showed intergranular crack initiation, mixed early propagation and a trend toward transgranular SCC as the crack propagated into the specimens. Additionally, a Cr-rich, faceted corrosion product was observed on the specimen surfaces and the crack density was markedly increased.

On duplex welded samples, crack initiation occurred in the δ - γ phase boundaries and cracking also became mixed intercellular/transgranular as the crack advanced, becoming totally transgranular near the overload failure region. These samples also exhibited a Cr-rich deposit. However, rather than the faceted crystals observed on annealed steels, the deposits appeared as mounds covering the mouths of surface-connected cracks. It is presently believed that these products are redeposited from the solution after corrosion has progressed and probably deposit at cathodic sites on the alloy surfaces.

The results of this investigation have formed the basis of a manuscript which is being prepared for presentation at a joint European conference on

electrochemical test methods for SCC evaluation to be held at Firminy,
France in September 1978 (abstract attached).

All preprints Removed

TABLE I

304 (Annealed)

100 ppm Cl^- , < 1 ppb O_2

AgCl ϕ	Test	%Strain	% Loss in Strain	% R.A.	% Loss in R. A.	ksi σ_{max}	% Loss in σ_{max}
ϕ_c	R15	32.7	base line	-52	base line	52.8	base line
-100	R34	14.5	-56	-16.9	-68	32.1	-39% loss
0	R35	10.6	-68	-18.6	-64	26.8	-49
+100	R25	22.6	-31	-28.5	-45	59.6	+13
+200	R33	9.7	-70	-31.8	-39	31.9	-40
+300	R27	8.0	-76	- 8.1	-84	20.2	-62
+500	R31	6.9	-79	- 5.1	-90	15.1	-71

TABLE II

304 Weldment

100 ppm Cl^- , < 1 ppb O_2

AgCl ϕ	Test	%Strain	% Loss in Strain	% R. A.	% Loss in R. A.	ksi σ_{max}	% Loss in σ_{max}
ϕ_c	R12	31.9	base line			67.3	base line
-200	R24	25.8	-19	-65	base line	64.0	- 4.9
-100	R29	11.1	-65	-29.9	-54	37.9	-44
0	R20	7.0	-78	-20.4	-69	30.1	-55
+100	R32	6.3	-80	- 5.4	-92	20.3	-70
+300	R28	10.6	-68	-12.9	-80	38.5	-43
+500	R30	10.5	-67	-26	-60	38.4	-42