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

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TECHNICAL PROGRESS REPORT

Pitting Corrosion

Potentiodynamic and galvanokinetic experiments have been performed on as-received and welded specimens of 304L stainless steel in 1N NaCl as a function of pH to determine the effect of retained ferrite on weld metal pitting behavior. Another goal of these experiments was to evaluate electrochemical techniques for determining repassivation potentials of as-received and welded samples. Welded samples were prepared by a series of overlapping parallel passes. Approximately 8% retained ferrite was observed in the welded specimens.

Results obtained from these experiments indicated that the critical pH for pitting protection is lower for weld metal than for as-received material. Protection from pitting is observed at pH 8.5 for the weld metal versus 11.5 for as-received materials. The latter data agrees with previously published data¹. The critical pitting potential was observed to be constant at all pH's lower than the critical pH value, although the morphology and density of pits changes with pH values for weld metal samples. As-received materials exhibited approximately the same pit density and morphology throughout the pH range studied with a high density of pits being observed, especially on the short transverse faces of the sheets. Welded samples below the critical pH showed a much lower density of very large pits which appear to nucleate at the ferrite/austenite phase

boundary. At $\text{pH} > 8.5$ pit density increased markedly. Pitting was primarily confined to the large flat faces of the samples with little or no attack on sample edges. While both as-received and welded specimens showed pit growth by means of a "cavern" process (only small surface perforations with large pits growing under a thin metal skin) this phenomenon was considerably more pronounced in the welded materials. As has been previously reported, pit nucleation in weldments occurs at more noble potentials than unwelded material, however the slope of the polarization curves ($\frac{\partial i}{\partial \phi}$) was shallower, indicating a lower activation energy for pit propagation.

A comparison of potentiokinetic and galvanokinetic experiments indicates that re-passivation potentials are not reproducible using potentiostatic scanning due to the geometry and distribution of pits formed in the active-noble scanning process. Critical pitting potentials were accurately measured using potentiokinetic tests and the two types of experiments need to be performed to obtain both critical pitting and re-passivation potentials. Another result of these experiments which has not previously been reported is a shift in solution pH for long time (low scan rate) tests. A shift in pH of two units in the basic direction (8-9 \rightarrow 10-11) was observed at the end of a 24-hour test. These results indicate that re-passivation potentials obtained after long term testing cannot be expected to be accurate.

A technical report on these pitting results is currently in preparation.

In addition to conducting pitting experiments in 1N NaCl, a high temperature autoclave testing system has been constructed to perform experiments in high purity water containing parts per million chloride ion and parts per million oxygen at 290°C. This system is constructed of titanium and has been instrumented for electrochemical experiments with the inclusion of an Ag-AgCl reference electrode. The system is currently in the process of being checked out and will be operational approximately 1 April 1976.

Stress Corrosion Cracking

Slow strain rate stress corrosion cracking tests of as-received and welded 304L and 304 stainless steel have been conducted in MgCl₂ at boiling points from 123 to 154°C (controlled by concentration). Corrosion potentials were monitored throughout the tests. Strain rates were varied from $1.6 \times 10^{-6} \text{ sec}^{-1}$ to $8.5 \times 10^{-4} \text{ sec}^{-1}$. Test results were compared to tests at equivalent temperatures in liquid paraffin.

In boiling 35% MgCl₂ (B.P.-123°C) decreasing strain rates led to decreased resistance to stress corrosion cracking of the as-received steels (shorter failure times, reduced ultimate tensile stresses and smaller elongations to failure). The stress corrosion cracking effect is no longer observed at strain rates in excess of $\frac{d\epsilon}{dt} \approx 4 \times 10^{-5} \text{ sec}^{-1}$. As expected, increasing temperatures has led to lowered stress corrosion cracking resistance ($\frac{d\epsilon}{dt} \approx 1.6 \times 10^{-5}$

sec^{-1}). Additionally, it was observed that 304L stainless steel exhibited intergranular failure at temperatures below 135°C but exhibited transgranular failure at 154°C . Corrosion potentials of the steels showed a marked decrease when yielding occurred, stabilized at a constant potential throughout plastic deformation and initial cracking, and exhibited a further pronounced drop in potential upon failure.

Two welded specimen configurations were examined: (1) a specimen containing a single transverse weld oriented normal to the tensile stress and (2) a specimen which was subjected to a series of overlapping weld passes and so consisted entirely of weld metal. When tested in liquid paraffin, the specimen containing the single transverse weld failed in the heat affected zone adjacent to the fusion zone. In boiling MgCl_2 at 135°C however, the failure occurred in the fusion zone and no cracking was observed outside of this zone.

In the all-weld-metal specimen failure occurred in the interphase boundaries at all temperatures. The stress corrosion cracking resistance of the all-weld-metal specimen was slightly inferior to as-received material.

The preferential cracking of the interphase boundary is thought to be due to non-equilibrium segregation of solute elements, particularly Cr, during the weld solidification. Experiments are currently being conducted to examine this hypothesis.

The susceptibility of welded materials to other hot Cl^- solutions

has also been examined. Boiling saturated NaCl solutions (B.P.= 107°C) at $\dot{\epsilon} = 1.7 \times 10^{-6}$ cm/cm/sec. to 5×10^{-4} cm/cm/sec. These experiments have shown that only at pH < 2.5 is as-received material susceptible to stress corrosion cracking and only at the slowest strain rate. All weld metal samples were only susceptible to stress corrosion cracking at pH < 1 and again, only at the slowest strain rate. Either H₂SO₄ or HCl and NaCl is effective in inducing susceptibility.

A slow strain rate test apparatus has been constructed which is capable of strain rates from 10^{-7} cm/cm/sec to 0.2 cm/cm/sec. This unit has been built around an autoclave for high temperature testing (290°C) and is instrumented for electrochemical measurements during testing. Calibration tests are currently underway and the unit will be operational on or about 1 April 1976.

1. H. P. Leckie, JECS, 117, 1153 (1970).

Principal Investigators' Effort on Project

	Academic Year	Summer
1 June 1975 - 29 February 1976 Dr. W. F. Savage	25%	35%
Dr. D. J. Duquette	10%	35%
1 March 1976 - 31 May 1976 Dr. W. F. Savage	25%	35%
Dr. D. J. Duquette	10%	N.A.