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EXPERIMENTS ON THE CORROSION OF 316 STAINLESS STEEL BY LIQUID LITHIUM

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ABSTRACT

A forced convection loop is used to study the corrosion of 316 stainless steel by liquid lithium at temperatures relevant to fusion reactors. Weight loss data are reported for tubular samples located in the hot zone of the loop. Temperatures of 440 C and 490 C have been used in the hot zone with temperature differences of 100 C to 200 C between the hot and cold zones. The effect of lithium velocity on local mass transfer rates is examined by simultaneously exposing stainless steel samples to parallel streams of lithium at velocities ranging from 40 to 130 cm/s. The loss rates become essentially steady after one month of exposure. The loss rate increases with lithium velocity in a manner suggestive of liquid-phase-controlled mass transfer.

INTRODUCTION

Liquid metals, because of their low vapor pressure and high thermal conductivity, are excellent heat transfer fluids. Their stability under radiation makes them especially attractive for nuclear reactor applications.

Fusion reactors operating on the D-T cycle must have lithium in the blanket region around the burning plasma in order to be self sufficient with respect to tritium. The lithium can be provided in elemental form, or as a eutectic or compound. For liquid systems, such as we consider here, the problems of corrosion and mass transport have to be addressed.

There are two major concerns related to corrosion and mass transport in a fusion reactor:

1 - Corrosion or dissolution of the liquid metal containing structure, and consequent change in its mechanical properties.

2 - Deposition of radioactive corrosion products in the cold zones of the loop, with consequent heat exchanger fouling and other related problems.

In the early days of conceptual fusion design studies it was generally believed that the first generation of fusion power reactors would have stainless steel as the structural material in the blanket and first wall. Experience with fission reactors had provided a wealth of data on 316 stainless steel, especially with respect to radiation damage. The ductility loss due to radiation damage would apparently limit the service life of the first wall to 2 or 3 years if 10% cold-worked 316 SS were used in a fusion reactor with a wall loading of 3-4 MW/m².

Many of the early conceptual designs had pure liquid lithium as the coolant and breeding material.  At that time there were no long-term, high temperature
data on the corrosion of 316 SS by liquid lithium under forced convection conditions. Short term tests gave extremely high corrosion rates, which implied that tons per year of radioactive corrosion products would be transported within the primary coolant loop. Furthermore, little was known about the effects of velocity on the corrosion process.

For the present study, a forced convection loop was built to investigate the long-term corrosion of 316 SS by lithium at conditions relevant to fusion reactors. Construction of the loop started in early 1976; testing began in August 1978 and continues at the present time.

**DESCRIPTION OF LOOP**

The loop consists of five major components: the main heater, the test zone, the economizer, the cooler, and the electromagnetic pump. A schematic of the loop is shown in Figure 1.

A conduction-type alternating current electromagnetic pump drives the lithium at a rate of 6 liters/min. The lithium first goes through the main heater where sufficient energy is supplied to make up for the heat rejected in the cooler and for the conduction and convection losses sustained around the loop. The main heater rated at 10 kW consists of a tube heater by clam shell temperature elements. It raises the lithium temperature about 20 C. A thermocouple just downstream of the heater modulates the power in the last clam shell heating element to control the lithium temperature. A manifold immediately downstream of the heater distributes the flow to the four test sections. Each test section has a valve and an electromagnetic flow meter to control and measure the lithium velocity.

The test zone is designed to be isothermal. It is contained in an insulated box with guard heaters on the outer surface. After going through the test zone the lithium is reunited in a manifold and enters the economizer. A surge tank, attached to the manifold, provides expansion space and a free surface from which to control the system pressure.

The surge tank has level detectors and is pressurized with high purity argon gas. As the lithium passes through the economizer (a counterflow heat exchanger) its temperature is reduced about 180 C and it loses an additional 20 C in the cooler. The cooler consists of four passes of finned pipes provided with an air blower. As it turns out, natural convection and radiation give sufficient cooling. A cold trap is provided downstream of the cooler. It consists of a dead-ended pipe which is
not insulated at the closed end. From the cooler, the lithium goes back through the economizer to the EM pump.

The loop is designed to allow the removal and reinsertion of the test coupons without draining the lithium. Each test section has a vertical extension with two ball valves in series. During operation, the upper part of the lithium in the vertical extension is frozen under cover of argon gas. When test coupons are being removed or reinserted, the EM pump is turned off, the frozen plugs are melted and a small portion of the lithium is drained into the dump tank in order to provide a slightly larger distance between the liquid level and the lower ball valve.

The test coupons are cut from 0.52 cm ID 316 SS tubing with a wall thickness of 0.9 mm. They are machine ground in a fixture to a length of 2.54 cm. When the coupons are stacked coaxially, they form a continuous tubular surface. It is extremely important that the coupons fit snugly into the split tube holder. A snug fit ensures a smooth inside wall, and thus gives better-defined flow conditions.

Each test section contains 16 coupons held together by a 45 cm long split tube with an OD of 1.27 cm. The coupons are numbered on the outer surface so that they can be reassembled in the same order every time. Figure 2 shows these parts in various stages of assembly.

FIGURE 2 The Test Coupons and Holders in Various Stages of Assembly

The loop is constructed entirely of 316 SS. It was welded by certified personnel and each weld was radiographed. The components were cleaned according to the procedure for ultra-high vacuum systems. After assembly, the loop was cleaned once again and leak tested on a mass spectrometer.

Trace heaters are strategically placed on all the loop components. These heaters are used continuously but are especially needed during shutdowns to keep the lithium from freezing.

Chromel-alumel thermocouples are used. There are more than 100 couples on the loop. The junctions are spot welded directly to the loop and ceramic beads are used to insulate the wires.

Diatomaceous silica was used to insulate most of the loop. Two one-inch
layers were used on the piping, except for the economizer, where fiberglass insulation was used on the outer layer.

Instrumentation and control systems were designed to allow automatic operation. The control system puts the loop onto a standby condition if operating limits of temperature, lithium level or electric power input were exceeded.

The output of the electromagnetic flow meters and selected thermocouples was continuously monitored and recorded. The lithium level in the surge tank was recorded manually.

TEST PROCEDURE AND METHODOLOGY

The electromagnetic flow meters were calibrated individually by gravity flow through each test section. The drainage rate was measured by use of a timer and the level detector. These tests agreed fairly well with thermal tests which included measuring the temperature rise of lithium pumped through the main heater at a known electrical power input. The valves in the test legs were then adjusted to provide the following velocities: 1.36 m/s, 0.96 m/s, 0.65 m/s and 0.45 m/s.

The experiment is intended to approximate the thermodynamic conditions which would be encountered in a lithium cooled fusion reactor. In a fusion reactor, the lithium going through the blanket would be heated to a high temperature and then would go to a heat exchanger. The test zone in the experiment simulates the fusion reactor blanket, while the radiator simulates the heat exchanger.

To determine the corrosion rate, the coupon assemblies are removed from the loop periodically. Removal and reinsertion of the four assemblies was usually accomplished within two days, once the techniques were mastered. Periods between coupon removal ranged from four to six weeks. Each time the coupons were removed, they were thoroughly cleaned of all residual lithium and then weighed on a precision balance. They were then reassembled in the same order and returned to the loop to continue the test.

The initial test, at a coupon temperature of 440 C and a minimum temperature of 255 C, lasted about 170 days. It was followed by a second test of 160 days with the same coupon temperature, but with the minimum temperature raised to 340 C. For the final test, which lasted 120 days, the coupon temperature was raised to 490 C and the minimum temperature was set at 325 C.

The coupon assemblies are removed in the following manner. An extension pipe is attached to the upper ball valve to provide a place for the assembly after removal from the loop. The space between the frozen lithium plug and the upper ball valve is evacuated and back-filled with argon. The frozen plug is then melted and the lithium level in the loop is lowered slightly. This is followed by equalization of the pressures in the surge tank and in the spaces above the test sections. Removal of the assembly is accomplished by means of a stainless steel fishing rod.
which is inserted through the two ball valves and is attached to the assembly by a threaded coupling. Once the assembly is lifted from the test section, the two ball valves are closed and the assembly is cooled in the extension pipe. During assembly removal, the extension pipe is purged with argon to shield the molten lithium. The cooled assembly is removed from the extension pipe and inserted into water to dissolve the residual lithium. After weighing, the coupons are reassembled in the same order. The assembly and extension pipe are then heated and purged with argon. The assemblies are returned to the loop through the two ball valves in each test section. The lithium level is then raised to the original point and the freeze plugs are reestablished.

During the initial filling of the loop, the lithium was hot trapped with zirconium at 500 °C and titanium at 650 °C. Lithium samples were taken after the hot trapping, and periodically during the tests. Several analyses are given in Table I.

The analyses provided by the vendor for the coupon materials are given in Table II. Heat 1 was used in the 440-255 C and 440-340 C tests, while Heat 2 was used in the 490-325 C test.

### TABLE I. LITHIUM ANALYSES

<table>
<thead>
<tr>
<th></th>
<th>After Hot Trapping</th>
<th>6 months at 440-255 C</th>
<th>1 month at 490-325 C</th>
<th>3 months at 490-325 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>453 ppm</td>
<td>50 ppm</td>
<td>85 ppm</td>
<td>120 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>-</td>
<td>-</td>
<td>5 ppm</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Chromium</td>
<td>-</td>
<td>-</td>
<td>10 ppm</td>
<td>4 ppm</td>
</tr>
<tr>
<td>Nickel</td>
<td>-</td>
<td>-</td>
<td>&lt; 5 ppm</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-</td>
<td>275 ppm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

Typical data on mass loss versus time are shown in Figure 3. The time scale of the graph begins with the onset of operation at 440 C coupon temperature after a month of calibration tests at lower temperatures.

![Figure 3: Total Mass Losses as a Function of Exposure Time](image)

The data for the 440 C coupon temperature are well fitted by straight lines after the first time interval; the
TABLE II. (316 SS ELEMENTAL ANALYSES)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat 1</td>
<td>17.15</td>
<td>11.4</td>
<td>2.1</td>
<td>1.76</td>
<td>0.42</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
<td>Superior Tube</td>
</tr>
<tr>
<td></td>
<td>16.36</td>
<td>11.75</td>
<td>2.39</td>
<td>1.65</td>
<td>0.63</td>
<td>0.06</td>
<td>0.02</td>
<td>0.01</td>
<td>Allegheny</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ludlom</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pacific Tube</td>
</tr>
</tbody>
</table>

slopes of these lines give the long-term asymptotic mass fluxes. A faster mass loss occurs over the first time interval according to these data (with the calibration period neglected), and is also observed with replacement coupons which start out at the test conditions.

This time pattern of mass loss is similar to that found by other workers (Whitlow et al 1979; (4) Tortorelli and DeVan 1979). (5) Tortorelli and DeVan attribute the rapid initial corrosion to depletion of Ni from the outer layer of the stainless steel.

Data from the current run at 490 C coupon temperature are also shown on Fig. 3. The earlier weighings at this temperature clearly show the higher initial corrosion rate.

Mass loss data similar to those in Figure 3 were simultaneously generated (for x/D from 6 to 70) for all four velocities. The approximate dissolution rates are given in Table III along with data from other sources. (3,4,5,6) An estimated rate is reported for the current run at 490 C coupon temperature. The most recent data here indicate that the long term mass loss rate may be somewhat lower than the estimated value.

Figure 4 shows the position dependence of the local mass fluxes. Each point is calculated by linear regression of the coupon weighings over an interval of several months. The dissolution mass flux decreases initially with downstream position x/D in each test section. This downward trend then gives way to fluctuations. For the two higher velocities, the point at which the fluctuations appear is at a length Reynolds number (DV/nu)(x/D) of approximately 4 x 10^5 (at the lower velocities, this point is beyond the range of x/D studied). This behavior suggests that the flow in the test sections is initially laminar, or is laminarized by the acceleration through the contraction @ x/D = 0. The fluctuations beginning at (xV/nu)=4x10^5 are attributed to the onset or resumption of turbulent flow.

Figure 5 shows the influence of lithium velocity on the mean mass flux, $\tilde{n}$, for the region from x/D=6 to 30. This region, comprising the first six coupons of each set, lies in the laminar region according to Figure 4. The data are fitted with lines according to the form

$$\tilde{n} = a(T) \nu^m.$$  (1)

The resulting exponents, m, range from 1/2 to 1/4.

For fluid-phase-controlled mass transfer in turbulent flow, the expected exponent in Equation 1 would be about 0.8. The appearance of a significantly lower value
### Table III - Corrosion of Type 316 Stainless Steel by Liquid Lithium

<table>
<thead>
<tr>
<th>Lab</th>
<th>I_max°C</th>
<th>I_min°C</th>
<th>ΔT°C</th>
<th>Time, hr</th>
<th>V/ms⁻¹</th>
<th>μg m⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>UW</td>
<td>440*</td>
<td>255</td>
<td>195</td>
<td>4000</td>
<td>1.4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>440*</td>
<td>340</td>
<td>110</td>
<td>3800</td>
<td>1.4</td>
<td>.85</td>
</tr>
<tr>
<td></td>
<td>490*</td>
<td>325</td>
<td>175</td>
<td>2900</td>
<td>1.4</td>
<td>7 (tentative)</td>
</tr>
<tr>
<td>Ward²⁴</td>
<td>538</td>
<td>386</td>
<td>152</td>
<td>1000</td>
<td>1.82</td>
<td>8</td>
</tr>
<tr>
<td>Whitlow (1979)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syracuse²³</td>
<td>590</td>
<td>545</td>
<td>45</td>
<td>&lt; 100</td>
<td>.8</td>
<td>6</td>
</tr>
<tr>
<td>Gill²² (1960)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORNL²⁵</td>
<td>600</td>
<td>450</td>
<td>150</td>
<td>3000</td>
<td>.03</td>
<td>3.5-5.5 (nat. conv.)</td>
</tr>
<tr>
<td>Tortorelli &amp; Devan (1979)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JAERI²⁶</td>
<td>600</td>
<td>500</td>
<td>100</td>
<td>2500</td>
<td>nat. conv. 3</td>
<td></td>
</tr>
<tr>
<td>Nihii (1974)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Coupon temperature; the maximum temperature is 10°C higher.
** Type 304 stainless steel.

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of m here is a further indication that the flows have been temporarily laminarized upon entering the test section. For developing laminar flow, an exponent of 1/2 would be expected; the exponent for the data at 440-255°C is actually 0.44. Mass transfer into a developed laminar flow would show a 1/3-power dependence on velocity; the 440-340°C and 490-325°C tests are nearer to this dependence.

The velocity dependence and position dependence of the mass flux show that fluid mechanics play a major role in the corrosion process. However, a full quantitative explanation of the data remains to be given. The following points merit further study:

1. The mass fluxes shown in Figure 5 are more than an order of magnitude lower than that predicted by boundary layer theory and an extrapolation of the solubility data of Leavenworth *et al.*²⁷

2. The velocity dependence in Fig. 5 is weaker than that predicted for a well-mixed condition at x=0. It is difficult, at this time, to describe the conditions at x=0 in any greater detail.

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**Summary and Conclusions**

A forced convection loop has been used to study the long-term corrosion of 316 stainless steel by liquid lithium at temperatures of 440°C and 490°C, temperature differences of 110°C to 195°C, and velocities of 40 cm/s to 130 cm/s.

The corrosion rates observed at 490°C with a temperature difference of 175°C...
FIGURE 4 Mass Loss Rates as a Function of Downstream Position are almost an order of magnitude higher than at 440°C with a temperature difference of 110°C. We conclude that 316 stainless steel fusion blankets using flowing liquid lithium at temperatures greater than 440°C will have serious difficulties with corrosion and redeposition of the structural material.

The velocity and position dependence of the mass flux indicate that fluid mechanics play a major role in the corrosion process. Low velocities, and laminar flow, should be used in the blanket region of fusion systems that employ liquid lithium as coolant.

FIGURE 5 Average Mass Fluxes as a Function of Velocity

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REFERENCES


2. B. Badger, et al., "UNMAK-III, A Non-


