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AUTHOR
Roy F. Maness

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# CORROSIVITY OF THORIA DISSOLVENT SOLUTIONS

By

Roy F. Maness
Chemical Development Section
Chemistry Department

Classified by: A. M. Platt



PACIFIC NORTHWEST LABORATORY
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# CORROSIVITY OF THORIA DISSOLVENT SOLUTIONS

## INTRODUCTION

The dissolution of thoria requires a fluoride-catalyzed nitric acid solution which is quite corrosive to most materials of construction. Aluminum nitrate is usually added to the dissolvent to reduce the hydrofluoric acid activity and thus the corrosivity of the system. As dissolution of thoria proceeds, Th(IV) forms a complex with fluoride ion which further reduces the corrosivity of the system. Corrosion tests of 304L stainless steel, Corronel 230, and HAPO-20 alloy were made in proposed thoria dissolvent solutions. The primary variables were nitric and hydrofluoric acid concentration, the presence of oxidants in the dissolvent and the metallurgical condition of the test specimens. Observed corrosion rates are presented in this report.

## RESULTS AND CONCLUSIONS

1. Of the three alloys tested (304L, Corronel 230, HAPO-20), Corronel 230 was the most corrosion resistant to solutions suitable for the dissolution of thoria.
2. The corrosivity of the dissolvents decreased as thoria dissolution proceeded due to a decrease in hydrofluoric acid concentration and to a decrease in nitric acid content.
3. The presence of oxidants (Cr[VI] and Fe[III]) in thoria dissolvents markedly increased the corrosivity to all alloys tested.
4. The corrosivity of the system $HNO_3$-HF-$Al(NO_3)_3$ increased significantly as the nitric acid content of the dissolvent was increased above 12.5 molar.
5. Weldments of the three alloys showed no preferential attack after exposure to 12.5M $HNO_3$-0.025M $NH_4F$-0.10M $Al(NO_3)_3$ solution for 480 hours.

6. Sensitization (one hour at 1250 F, water quenched) decreased the corrosion resistance of 304L to thoria dissolvent solutions by a factor of about ten. However, no sensitization effect was noted with 1/4- and 1/2-inch-thick weldments tested in the as-fabricated condition.

7. Severely corrosive conditions occur during concentration of the dissolver solution to remove nitric acid. Sensitized 304L specimens exposed to the vapor phase corroded at rates as high as 60 mils/month.

EXPERIMENTAL AND DISCUSSION

The compositions of the alloys tested are given in Table I. Corronel 230 is a product of Henry Wiggin and Co., Birmingham, England. HAPO-20 is an alloy developed locally to contain non-production reactor fuel dissolvents and is available only by special request. Weldments were prepared using the tungsten-inert gas process. Strips cut from the base metal were used as filler metal for HAPO-20 alloy. The 304L weldments were fabricated using 308L rod. A commercially available welding rod, essentially of base metal composition, was used to fabricate Corronel 230 weldments.

Corrosion test specimens were prepared by grinding all surfaces to a 120 grit finish and passivating in nitric acid solution. Weldments were ground only on the cut surfaces and were exposed briefly to a $HNO_3$-HF pickling solution prior to passivation. All test solutions were at the boiling point and were contained in Teflon bottles equipped with Teflon condensers. Fresh solution was added after each 48-hour exposure period. Corrosion rates were calculated for each period on the basis of weight loss. However, for most tests, only an overall average corrosion rate is reported. Data obtained in simple boiling tests and in tests under heat transfer conditions are given in Table II. It is apparent that, of the three alloys tested, Corronel 230 exhibited the greatest corrosion resistance. It is also apparent that the "standard" thoria dissolvent, initially 12.5M $HNO_3$-0.025M $NH_4F$-0.10M $Al(NO_3)_3$, is aequately contained by annealed or slightly

sensitized 304L or by HAPO-20 alloy. The corrosion resistance of 304L, after a one-hour heat treatment at 1250 F, is poor in thoria dissolvent solution. However, the metallurgical condition of 304L sensitized in this manner is probably not representative of the condition of 304L found in a fabricated production vessel. The sensitization effect produced in the fabrication of 1/2-inch-thick weldments was quite small. The sensitization effect was investigated further by determining the corrosion resistance of 304L to thoria dissolvent solution as a function of the heat treatment time at 1250 F. The results are given in Table III. The sensitization effect is significant when the time at temperature exceeds ten minutes. Corrosion rates of coupons exposed to the vapor phase were somewhat erratic, presumably because the precise position of the specimens with regard to the condenser determined the degree of contact with condensate.

The presence of Fe(III) and Cr(VI) (and presumably other oxidants) in thoria dissolvent solution is clearly to be avoided. Catastrophic corrosion of all alloys tested occurred when these materials were present at the 0.01M level.

Data obtained on the corrosivity of thoria dissolver solution during simulated concentration to remove excess nitric acid are given in Table IV. It is apparent that 304L in the sensitized condition (one hour at 1250 F, water quenched) suffers severe corrosion under these conditions. It is also apparent that as-fabricated weldments are only moderately attacked. Removal of excess nitric acid via concentration is definitely feasible using a material of construction with a corrosion resistance equivalent to that of Corronel 230 alloy. Chemical destruction of excess nitric acid prior to concentration would reduce greatly the corrosivity of the system.

TABLE I

ALLOY COMPOSITIONS

| Alloy | Weight Percent | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fe | Cr | Ni | Si | Mn | Ti | Cu | Mo | C |
| 304L | Bal. | 18.8 | 9.8 | 0.53 | 1.3 | - | - | - | 0.02 |
| Corronel 230 | 1.8 | 34.0 | Bal. | 0.30 | 0.3 | 0.13 | 0.01 | - | 0.04 |
| HAPO-20 | 16.0 | 25.0 | 50.0 | 0.4 | 0.6 | 1.0 | 1.0 | 6.0 | 0.02 |

## TABLE II

## CORROSIVITY OF THORIA DISSOLVENT SOLUTIONS

| Solution | Material (1) | Exposure Hours | Corrosion Rate Mils/Month Liquid | Corrosion Rate Mils/Month Vapor |
|---|---|---|---|---|
| 12.5M $HNO_3$-0.01M $NH_4F$-0.10M $Al(NO_3)_3$ | 304L | 480 | 7.0 | 5.2 |
| 12.5M " -0.025M " -0.10M " | 304L | 480 | 12.0 | 18.0 |
| 12.5M " -0.085M " -0.62M " -0.025M $Hg(NO_3)_2$ | 304L | 480 | 36.0 | 20.0 |
| 14.0M " -0.01M " -0.10M " | 304L | 480 | 28.0 | 22.0 |
| 8.5M " -0.025M " -0.10M " -1.0M $Th(NO_3)_4$ | 304L | 487 | 1.9 | 2.3 |
| 11.5M " -0.025M " -0.10M " -0.25M " | 304L | 240 | 1.6 | 1.2 |
| 15.2M " -0.01M " -0.10M " -$ThO_2$ dissolving to 1.0M | 304L | 24 | 0.9 | 1.2 |
| 14.4M " -0.01M " -0.40M " - " " " | 304L | 24 | 0.6 | 0.8 |
| 12.5M " -0.01M " -0.10M " -0.01M Cr(VI) | 304L | 210 | 73.0 | 16.0 |
| 12.5M " -0.01M " -0.10M " -0.05M Fe(III) | 304L | 210 | 15.0 | 24.0 |
| 11.2M " -0.01M " -0.10M " -1.0M $Th(NO_3)_4$ | 304L | 113 | 30.0 | 1.6 |
| 10.4M " -0.01M " -0.40M " -1.0M " | 304L | 113 | 15.0 | 1.5 |
| 12.5M " -0.01M " -0.10M " | 304L (Annealed) | 460 | 0.6 | 0.6 |
| 12.5M " -0.025M " -0.10M " | 304L (Annealed) | 460 | 1.2 | 1.4 |
| 12.5M " -0.01M " -0.10M " | 304L (1/4" weldment)(2) | 461 | 0.6 | - |
| 12.5M " -0.025M " -0.10M " | 304L (1/4" weldment)(2) | 461 | 1.1 | - |
| 12.5M " -0.025M " -0.10M " | 304L (1/2" weldment)(3) | 240 | 1.2 | - |
| 12.5M " -0.025M " -0.10M " | 304L (1/2" weldment)(4) | 240 | 1.5 | - |
| 12.5M " -0.01M " -0.10M " | 304L (Ht. Tr. - 135 C)(5) | 169 | 8.5 | 2.0 |
| 12.5M " -0.025M " -0.10M " | 304L (Ht. Tr. - 135 C)(5) | 162 | 14.0 | 1.0 |
| 15.5M " -0.01M " -0.10M " | 304L (Ht. Tr. - 140 C)(5) | 217 | 37.0 | 1.2 |
| 15.5M " -0.025M " -0.10M " | 304L (Ht. Tr. - 135 C)(5) | 217 | 19.0 | 2.0 |
| 8.5M " -0.025M " -0.10M " -1.0M $Th(NO_3)_4$-0.01M Cr(VI) | 304L | 210 | 13.0 | 1.4 |
| 11.2M " -0.01M " -0.10M " -1.0M " -0.01M Fe(III) | 304L | 90 | 21.0 | 1.2 |
| 10.4M " -0.01M " -0.40M " -1.0M " -0.01M Cr(VI) | 304L | 90 | 64.0 | 2.4 |
| 12.5M " -0.025M " -0.05M $Th(NO_3)_4$ | 304L | 120 | 18.0 | 11.0 |
| 12.5M " -0.025M " -0.10M " | 304L | 120 | 3.6 | 7.5 |
| 12.5M " -0.025M " -0.25M " | 304L | 120 | 2.6 | 1.6 |
| 12.5M " -0.01M " -0.10M $Al(NO_3)_3$ | HAPO-20 | 480 | 1.1 | 1.4 |
| 12.5M " -0.025M " -0.10M " | HAPO-20 | 480 | 1.7 | 1.1 |
| 12.5M " -0.085M " -0.625M " -0.025M $Hg(NO_3)_2$ | HAPO-20 | 480 | 1.9 | 1.2 |
| 14.0M " -0.01M " -0.10M " | HAPO-20 | 480 | 6.7 | 1.0 |
| 11.5M " -0.025M " -0.10M " -0.25M $Th(NO_3)_4$ | HAPO-20 | 240 | 0.5 | 0.4 |
| 12.5M " -0.01M " -0.10M " | HAPO-20(Ht. Tr. - 135 C)(5) | 169 | 1.8 | 1.1 |
| 12.5M " -0.025M " -0.10M " | HAPO-20(Ht. Tr. - 135 C)(5) | 162 | 2.8 | 2.0 |
| 12.5M " -0.025M " -0.10M " | HAPO-20(1/8" weldment) | 480 | 1.3 | - |

TABLE II (Continued)

CORROSIVITY OF THORIA DISSOLVENT SOLUTIONS

| Solution | Material[1] | Exposure Hours | Corrosion Rate Mils/Month Liquid | Vapor |
|---|---|---|---|---|
| 12.5M $HNO_3$-0.025M $NH_4F$ -0.10M $Al(NO_3)_3$-0.01M Cr(VI) | HAPO-20 | 120 | 30.0 | 0.7 |
| 12.5M " -0.025M " -0.10M $Al(NO_3)_3$ | Corronel 230 | 488 | 0.3 | 0.2 |
| 12.5M " -0.025M " -0.10M " | Corronel 230 (1/4" weldment) | 480 | 0.4 | - |
| 11.5M " -0.025M " -0.10M " -0.25M $Th(NO_3)_4$ | Corronel 230 (1/4" weldment) | 240 | 0.3 | 0.1 |
| 12.5M " -0.025M " -0.10M " | Corronel 230 (Ht.Tr.-135 C)[5] | 293 | 0.6 | - |
| 12.5M " -0.025M " -0.10M " -0.01M Cr(VI) | Corronel 230 | 144 | 16.0 | 0.3 |

NOTES:

(1) All materials in sensitized condition unless otherwise noted. Heat treated for one hour at 1250 F, water quenched.

(2) TIG produced weldment using 308L filler metal.

(3) MIG produced weldment using 308L filler metal. Carbon content of weld metal = 0.027 percent.

(4) MIG produced weldment using 308L filler metal. Carbon content of weld metal = 0.033 percent.

(5) Test under heat transfer conditions. Bulk metal temperature given.

## TABLE III

## EFFECT OF SENSITIZATION TIME ON 304L CORROSION RATES

**Conditions:** Five 48-hour exposures to boiling 12.5M $HNO_3$-0.025M $NH_4F$-0.10M $Al(NO_3)_3$ solution contained in Teflon.

**Liquid Phase**

| Time at 1250 F, Minutes | Corrosion Rate, Mils/Month — Period 1 | 2 | 3 | 4 | 5 | Avg. |
|---|---|---|---|---|---|---|
| 0 | 1.3 | 1.2 | 1.2 | 1.1 | 1.2 | 1.2 |
| 3 | 1.4 | 1.2 | 1.0 | 1.2 | - | 1.2 |
| 5 | 1.4 | 1.2 | 1.1 | 1.0 | 1.1 | 1.2 |
| 10 | 1.8 | 2.1 | 2.1 | 1.5 | 2.2 | 1.9 |
| 20 | 2.3 | 2.0 | 3.0 | 4.5 | 5.7 | 3.5 |
| 45 | 3.6 | 4.8 | 4.4 | 8.0 | 11.0 | 6.4 |
| 60 | 2.8 | 4.0 | 6.4 | 7.5 | 16.0 | 7.3 |
| 120 | 5.0 | 7.3 | 8.5 | 9.9 | 15.0 | 9.1 |

**Vapor Phase**

| | | | | | | |
|---|---|---|---|---|---|---|
| 0 | 1.3 | 1.3 | 1.3 | 1.0 | 1.3 | 1.2 |
| 3 | 1.3 | 1.5 | 2.5 | 3.2 | 4.2 | 2.5 |
| 5 | 1.3 | 1.5 | 1.4 | 1.2 | 1.3 | 1.3 |
| 10 | 1.8 | 1.8 | 1.9 | 2.3 | 2.1 | 2.0 |
| 20 | 1.5 | 1.8 | 1.9 | 3.3 | 3.5 | 2.4 |
| 45 | 2.5 | 1.3 | 3.4 | 5.2 | 5.6 | 3.6 |
| 60 | 9.1 | 8.3 | 11.0 | 18.0 | 12.0 | 12.0 |
| 120 | 11.0 | 7.2 | 8.3 | 8.2 | 8.3 | 8.6 |

TABLE IV

CONCENTRATION OF THORIA DISSOLVER SOLUTION

A. 304L Corrosion Rates

Conditions: Solution containing 8.5M $HNO_3$-0.025M $NH_4F$-0.10M $Al(NO_3)_3$ - 1.0M $Th(NO_3)_4$ concentrated four-fold in Teflon equipment. Condensate returned to bottoms and solution reconcentrated. Fresh solution every 16 to 24 hours.

Sensitized Specimens
(One hour at 1250 F)

| | Corrosion Rate, Mils/Month | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Accumulative Exposure Hours | | | | | | | |
| | 50 | 98 | 119 | 140 | 148 | 155 | 163 | 171 |
| Liquid Phase | 1.2 | 7.4 | 8.0 | - | 4.6 | 7.4 | 6.2 | 19.0 |
| Vapor Phase | 1.3 | 2.7 | 45.0 | 35.0 | 40.0 | 48.0 | 48.0 | 61.0 |

Weldments as Fabricated
(1/2" thick 304L plate)

| | 42 | 69 | 91 | 117 | 143 | 167 | 192 | 224 |
|---|---|---|---|---|---|---|---|---|
| Liquid Phase | 0.9 | 1.2 | 1.9 | 1.5 | 1.3 | 1.4 | 1.6 | 1.5 |
| Vapor Phase | 0.8 | 0.7 | 1.8 | 3.9 | 1.8 | 2.4 | 3.3 | 2.3 |

B. Corronel 230 Corrosion Rates

Conditions: As above. Corronel 230 weldments (as-fabricated) exposed to liquid phase. Sensitized coupons exposed to vapor phase.

| | Corrosion Rate, Mils/Month | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Accumulative Exposure Hours | | | | | | | |
| | 8 | 20 | 32 | 47 | 62 | 81 | 100 | 115 |
| Liquid Phase | 1.4 | 1.5 | 0.9 | 0.6 | 0.8 | 2.3 | 0.8 | 0.7 |
| Vapor Phase | 0.9 | 0.2 | 0.2 | 0.3 | 0.3 | 0.7 | 0.1 | 0.2 |