Corrosion Test Results for Construction Materials Used in Mini-SHINE System

Chemical Sciences and Engineering Division

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by

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CORROSION TEST RESULTS FOR CONSTRUCTION MATERIALS USED IN MINI-SHINE SYSTEM

1 INTRODUCTION

To satisfy Argonne safety requirements, we are using sodium bisulfate as a surrogate for uranyl sulfate during irradiation tests at the linac prior to conducting experiments with uranyl sulfate. After passing a 0.55 M NaHSO₄/0.1 M H₂SO₄ (pH 1) solution through the target solution vessel and stainless-steel tubing, valves, and pump as part of the mini-SHINE experimental setup at the linac, the solution turned blue. The blue color intensified when the system temperature reached 80 °C. The tubing and target solution vessel are made of 304SS, and all other components are made of 316SS. As a result, corrosion tests were performed using 304SS and 316SS in contact with H₂O, 0.1 M H₂SO₄, 0.55 M NaHSO₄, and 140 g-U/L UO₂SO₄ for 6 hours, 24 hours, 5 days, 10 days, and 30 days at 60°C and 80°C. Corrosion-rate data were required to ensure the sodium bisulfate, sulfuric acid (pH = 1), and uranyl sulfate (140 g-U/L) solutions would not corrode the components of the mini-SHINE setup to any great extent. Also subjected to these tests were 2205SS and Ti metal. The 2205SS was tested because it is similar to 2304SS, which is currently being tested at Oak Ridge National Laboratory. Oak Ridge is doing a more thorough set of corrosion tests for SHINE Medical Technologies. Titanium metal was tested as a blank to ensure metals such as Fe, Ni, and Cr did not stick to the discs that were made with a stainless steel punch.

2 MATERIALS AND METHODS

Discs (0.25-inch outer diameter) were cut from 1/16-inch-thick sheets of 304SS, 316SS, 2205SS, and Ti. Each metal disc was rinsed with ethanol to remove manufacturing oils and allowed to dry at room temperature. Each disc was placed in a test tube with a solution containing 4 mL of H_2O , 0.1 M H_2SO_4 , 0.55 M NaHSO_4 , or 140 g-U/L UO_2SO_4 (pH = 1). The tubes were covered by a vented slip-on cap. Samples were kept at 60°C and 80°C using thermostated baths (unit 1 – Thermo Scientific Model 2870 and unit 2 – Thermo-Haake Model SWB25, both with a 120 tube capacity) for 6 hours, 24 hours, 5 days, 10 days, and 30 days. After each time period, discs were removed from the test tube, washed with water, dried, and weighed to determine the corrosion rates based on changes in mass. Significant water losses occurred in the samples left at 60°C and 80°C for 30 days, so makeup water was added to the remaining solution after 30 days but before solutions were submitted for analyses. All solutions were submitted for inductively coupled plasma-mass spectroscopy (ICP-MS) analyses to determine the concentration of Fe, Ni, Cr, and Ti after contact with each metal disc.

3 RESULTS

Figures 1-3 show estimated corrosion rates in units of mm/year, and Figures 4-6 show estimated corrosion rates in units of mil/year for discs in contact with 0.1 M H₂SO₄, 0.55 M NaHSO₄, and 140 g-U/L UO₂SO₄. (These data are also given in tabular form in the appendix.) These corrosion rates show high initial values that eventually level off, indicating that a passivation layer has formed. However, the reported corrosion rates should be considered as estimates, as non-ASTM approved methods and techniques were employed in this study. The ICP-MS data agree with the estimated corrosion rates in that the Fe, Ni, and Cr concentrations did not increase to any great extent after initial corrosion was observed in the first 6–24 hours.

In general, the discs in contact with 0.1 M H₂SO₄ (Figures 1 and 4) have lower estimated corrosion rates than the discs that were contacted with 0.55 M NaHSO₄ (Figures 2 and 5) and 140 g-U/L UO₂SO₄ (Figures 3 and 6). The 316SS samples show the highest initial corrosion rates after 6 and 24 hours of contact with 0.1 M H₂SO₄ (Figures 1 and 4); however, after 10 days, the estimated corrosion rates decrease significantly. Estimated corrosion rates for all samples in contact with 0.1 M H₂SO₄ become negligible after 10 days. Sodium bisulfate is the most corrosive solution as it has the highest concentration of free sulfate. Titanium metal is most affected by 0.55 M NaHSO₄ (Figures 2 and 5) where corrosion rates at 80°C do not fall below 3 mm/yr (~0.12 mil/yr). Both 304SS and 316SS show corrosion rates at 80°C of 1-1.2 mm/yr (~0.5 mil/yr) after contact with 0.55 M NaHSO₄, but those rates decrease to 0.5 mm/yr (~0.02 mil/yr) after 30 days. Uranyl sulfate is slightly more corrosive than 0.1 M H₂SO₄, but corrosion rates are below 0.05 mm/yr (0.02 mil/yr) for all discs after 30 days (Figures 3 and 6).

FIGURE 1 Estimated corrosion rates in units of mm/yr for discs in contact with 0.1 M H₂SO₄ at 60°C and 80°C

FIGURE 2 Estimated corrosion rates in units of mm/yr for discs in contact with 0.55 M NaHSO₄ at 60°C and 80°C

FIGURE 3 Estimated corrosion rates in units of mm/yr for discs in contact with 140 g-U/L UO₂SO₄ at 60°C and 80°C

FIGURE 4 Estimated corrosion rates in units of mil/yr for discs in contact with 0.1 M H₂SO₄ at 60°C and 80°C

FIGURE 5 Estimated corrosion rates in units of mil/yr for discs in contact with 0.55 M NaHSO₄ at 60°C and 80°C

FIGURE 6 Estimated corrosion rates in units of mil/yr for discs in contact with 140 g-U/L UO_2SO_4 at 60°C and 80°C

Figure 7 shows the concentration of Fe present in all solutions after being in contact with 304SS discs for 0.25–30 days at 60°C and 80°C. Iron concentrations are the highest after contact with NaHSO_4 at 80°C for periods greater than one day. After 10 days of contact in all solutions, the concentration of Fe did not increase to any great extent. For samples in contact with UO_2SO_4 solutions, the Fe concentration is only slightly higher at 80°C compared to 60°C. Concentrations of Fe and Ti measured in the blank solutions before contact with the discs were subtracted from the ICP-MS values obtained after contact with the various solutions.

Figure 8 shows the concentration of Fe present in all solutions after being in contact with 316SS discs for 0.25–30 days at 60°C and 80°C. With sodium bisulfate at 80°C, Fe concentration is the highest after contact with 316SS, increasing rapidly in the first ten days then stabilizing. After 10 days of contact, the concentration of Fe does not increase significantly for all solutions except 0.1 M H_2SO_4 at 80°C, in which the Fe concentration increases from 10 to 30 days, but decreases from 5 to 10 days. By contrast, the Fe concentration remains unchanged after extended contact with 0.1 M H_2SO_4 at 60°C. For samples in contact with uranyl sulfate solutions, the concentration of Fe does not increase over the entire test period and is only slightly higher at 80°C, which is consistent with the 304SS results.

Figure 9 shows the Fe concentration present in all solutions after being in contact with 2205SS discs for 0.25–30 days at 60°C and 80°C. The Fe concentration is the highest after contact with uranyl sulfate solutions at 60°C and 80°C, but that is consistent with results obtained with 304SS and 316SS, where the concentration is near $1 \times 10^5 \mu\text{g/L}$ Fe. Because 2205SS is more robust than 304SS and 316SS, it shows less corrosion in the presence of pH 1 sulfuric acid and sodium bisulfate.

Figure 10 shows the concentration of Ti present in all solutions after being in contact with Ti discs for 0.25–30 days at 60°C and 80°C. The Ti concentration is the highest after

FIGURE 7 Iron Concentration in Various Solutions after Contact with 304SS Discs for 0.25–30 Days at 60°C and 80°C

FIGURE 8 Iron Concentration in Various Solutions after Contact with 316SS Discs for 0.25–30 Days at 60°C and 80°C

FIGURE 9 Iron Concentration in Various Solutions after Contact with 2205SS Discs for 0.25–30 Days at 60°C and 80°C

FIGURE 10 Titanium Concentration in Various Solutions after Contact with Ti Discs for 0.25–30 Days at 60°C and 80°C

contact with sodium bisulfate solutions at 60°C and 80°C. There is a large increase in Ti concentration after contact with UO_2SO_4 at 80°C from 10-30 days, which indicates that Ti metal may continue to corrode in this type of environment and not form a passivation layer.

Figures 11 and 12 show the Fe concentration present in a 0.1 M H_2SO_4 solution at 60°C and 80°C, respectively, after contact with each type of metal disc. Results indicate that the Ti metal has Fe in it because Fe was present in solution after contact with 0.1 M H_2SO_4 , and only 28 µg/L was found in the blank acid solution. The 316SS samples had the highest Fe concentration after contact with pH 1 sulfuric acid at 60°C and 80°C. Still, the concentration of Fe in solution for most samples begins to plateau, or even decrease slightly, after 10 days of contact.

Figures 13 and 14 show the Fe concentration present in a 0.55 M NaHSO_4 solution at 60°C and 80°C, respectively, after contact with each type of metal disc. Results indicate that the Ti metal has Fe in it because Fe was present in solution after contact with Ti metal, but no detectable Fe was present in the blank sodium bisulfate solution. The 316SS samples have the highest Fe concentration after contact with sodium bisulfate at 60°C, and at 80°C, the concentration of Fe present in the 316SS and 304SS samples is almost identical. Still, the concentration of Fe in solution for all samples levels off after 10 days of contact.

Figures 15 and 16 show the Fe concentration present in a 140 g-U/L UO_2SO_4 solution at 60°C and 80°C after contact with each type of metal disc. The ICP-MS results indicate that the uranyl sulfate solution contains 6.0×10^4 mg/L Fe, but the Ti metal also contains Fe based on the corrosion test results with sulfuric acid and sodium bisulfate. The amount of Fe found in the blank solution was subtracted from the amount of Fe found in each sample after contact with uranyl sulfate. As shown in the figures, Fe concentrations increase steadily in all samples over time at 60°C and decrease slightly from 10-30 days at 80°C, but concentrations never exceed 4.5×10^4 µg/L Fe.

FIGURE 11 Iron Concentration in 0.1 M H_2SO_4 Solution after Contact with SS and Ti Discs for 0.25–30 Days at 60°C

FIGURE 12 Iron Concentration in 0.1 M H₂SO₄ Solution after Contact with SS and Ti Discs for 0.25–30 Days at 80°C

FIGURE 13 Iron Concentration in 0.55 M NaHSO₄ Solution after Contact with SS and Ti Discs for 0.25–30 Days at 60°C

FIGURE 14 Iron Concentration in 0.55 M NaHSO₄ Solution after Contact with SS and Ti for 0.25–30 Days at 80°C

FIGURE 15 Iron Concentration in 140 g-U/L UO₂SO₄ Solution after Contact with SS and Ti Discs for 0.25–30 Days at 60°C

FIGURE 16 Iron Concentration in 140 g-U/L UO_2SO_4 Solution after Contact with SS and Ti Discs for 0.25–30 Days at 80°C

4 DISCUSSION

The purpose of this set of corrosion tests was to demonstrate to Argonne safety personnel that the mini-SHINE target solution vessel and entire system will not corrode enough to create serious problems. The ICP-MS and mass-change data indicate that the estimated corrosion rates are high at first but decrease to negligible levels once a passivation layer forms. Sodium bisulfate is the most corrosive solution of all those tested because the free sulfate concentration is much higher than in pH 1 sulfuric acid or uranyl sulfate solutions.

5 CONCLUSIONS

Discolored solutions were observed in our mini-SHINE system after it was contacted with pH 1 sulfuric acid and sodium bisulfate solutions. Corrosion tests were performed to assess the stability of the mini-SHINE construction materials, and all results indicate corrosion is not an issue once a passivation layer forms, which usually occurs within the first 24 hours. These results will be useful for SHINE because most of SHINE's plumbing will be 316SS. Corrosion in pH 1 sulfuric acid and uranyl sulfate solutions should not be a problem once a passivation layer forms.

APPENDIX A

DATA FOR CORROSION TESTS PERFORMED AT 60°C AND 80°C IN THE PRESENCE OF 304SS, 316SS, 2205SS, AND TITANIUM

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APPENDIX A

DATA FOR CORROSION TESTS PERFORMED AT 60°C AND 80°C IN THE PRESENCE OF 304SS, 316SS, 2205SS, AND TITANIUM

**TABLE 1 Data for Discs in contact with
0.1 M H₂SO₄ at 60°C and 80°C**

H ₂ SO ₄ 60°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	0.040	0.155	0.061	0.000
1	0.032	0.074	0.011	0.028
5	0.000	0.008	0.008	0.000
10	0.003	0.005	0.000	0.008
30	0.002	0.002	0.001	0.002
H ₂ SO ₄ 60°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.002	0.006	0.002	0.000
1	0.001	0.003	0.000	0.001
5	0.000	0.000	0.000	0.000
10	0.000	0.000	0.000	0.000
30	0.000	0.000	0.000	0.000
H ₂ SO ₄ 80°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	0.000	0.408	0.000	0.000
1	0.032	0.527	0.006	0.000
5	0.006	0.133	0.005	0.000
10	0.000	0.004	0.000	0.002
30	0.001	0.000	0.000	0.000
H ₂ SO ₄ 80°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.000	0.016	0.000	0.000
1	0.001	0.021	0.000	0.000
5	0.000	0.005	0.000	0.000
10	0.000	0.000	0.000	0.000
30	0.000	0.000	0.000	0.000

**TABLE 2 Data for Discs in contact with
0.1 M NaHSO₄ at 60°C and 80°C**

NaHSO ₄ 60°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	0.000	0.614	0.225	1.417
1	0.011	0.353	0.000	0.159
5	0.009	0.071	0.000	1.700
10	0.000	0.015	0.006	1.493
30	0.000	0.007	0.000	0.002
NaHSO ₄ 60°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.000	0.025	0.009	0.056
1	0.000	0.014	0.000	0.006
5	0.000	0.003	0.000	0.067
10	0.000	0.001	0.000	0.059
30	0.000	0.000	0.000	0.000
NaHSO ₄ 80°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	1.204	0.136	0.041	4.632
1	1.350	1.059	0.000	4.661
5	0.762	0.689	0.006	4.009
10	0.783	0.681	0.000	4.145
30	0.448	0.488	0.000	3.312
NaHSO ₄ 80°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.047	0.005	0.002	0.182
1	0.053	0.042	0.000	0.183
5	0.030	0.027	0.000	0.158
10	0.031	0.027	0.000	0.163
30	0.018	0.019	0.000	0.130

**TABLE 3 Data for Discs in contact with
140 g-U/L UO_2SO_4 at 60°C and 80°C**

UO_2SO_4 60°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	0.375	0.039	0.286	0.207
1	0.011	0.000	0.028	0.113
5	0.016	0.006	0.005	0.033
10	0.003	0.000	0.007	0.002
30	0.000	0.039	0.038	0.000
UO_2SO_4 60°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.015	0.002	0.011	0.008
1	0.000	0.000	0.001	0.004
5	0.001	0.000	0.000	0.001
10	0.000	0.000	0.000	0.000
30	0.000	0.002	0.002	0.000
UO_2SO_4 80°C				
Time (days)	304SS (mm/yr)	316SS (mm/yr)	2205SS (mm/yr)	Ti (mm/yr)
0.25	0.395	0.175	0.143	0.104
1	0.011	0.105	0.000	0.019
5	0.015	0.023	0.014	0.026
10	0.009	0.003	0.003	0.020
30	0.025	0.000	0.000	0.000
UO_2SO_4 80°C				
Time (days)	304SS (mil/yr)	316SS (mil/yr)	2205SS (mil/yr)	Ti (mil/yr)
0.25	0.016	0.007	0.006	0.004
1	0.000	0.004	0.000	0.001
5	0.001	0.001	0.001	0.001
10	0.000	0.000	0.000	0.001
30	0.001	0.000	0.000	0.000

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