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THE DISSOLUTION OF ZIRCONIUM AND
CORROSION OF STAINLESS STEEL IN
SULFURIC ACID AND NITRIC-
HYDROFLUORIC ACID MIXTURES

By
R. H. J. Gercke
D. Lewis

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Livermore Research Laboratory
California Research and Development Company
Livermore, California

Technical Information Service, Oak Ridge, Tennessee

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ABSTRACT

The dissolution of zirconium metal and the corrosion of several stainless steels were measured in both sulfuric acid and nitric-hydrofluoric acid mixtures. Zirconium metal is readily dissolved in 90 per cent sulfuric acid at 100C or higher. Dissolution rates are high in 20 per cent nitric - 3 per cent hydrofluoric acid mixtures at temperatures above 25C. Chlorimet 2 was found to have very good resistance to 86 per cent sulfuric acid at 100C but was unsatisfactory at 225C. Durimet 20 was estimated to be satisfactory at 100C. Of the stainless steels tested only 309-Cb and Durimet 20 have good corrosion resistance to 20 per cent nitric - 3 per cent hydrofluoric acid mixtures at 30C.

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INTRODUCTION

Because of its high corrosion resistance at high temperatures toward many coolants, and its low neutron capture cross section, zirconium metal is a potential cladding material for uranium or thorium elements in a reactor.

If these elements are to be prepared for Purex or other aqueous processing in order to recover product, a dissolving medium for these plates, as well as a suitable dissolver tank construction material must be found. Available information showed that it might be possible to dissolve the zirconium cladding leaving the uranium or thorium for the usual aqueous dissolving procedure, or it might be possible to dissolve both the cladding and uranium or thorium in the same medium. Based on available information, the dissolving media most likely to be used in the dissolution were thought to be (1) approximately 90 per cent sulfuric acid for cladding removal, and (2) nitric and hydrofluoric acid mixtures for integral dissolving.

It was indicated that for sulfuric acid duty the molybdenum steels gave good service. These would include the following stainless steels: 316, 317, 318, Durimet 20, Chlorimet 2, Pioneer alloys, and Hastelloys B and D. For nitric acid-hydrofluoric acid duty types 309, 309-Cb, 316 etc, 347, and Durimet 20 were indicated to be the most serviceable. The experimental work described in this report concerned itself with obtaining initial dissolving rates of zirconium metal in sulfuric acid and also nitric acid-hydrofluoric acid mixtures. Corrosion rates of a number of stainless steels in the same acids were obtained with a view to finding a suitable dissolver vessel construction material with the stipulation that a corrosion rate of 120 mils/yr should not be exceeded.

EXPERIMENTAL PROCEDURE & RESULTS

The dissolving rate of zirconium metal in 86, 90, and 96 per cent sulfuric acid was determined at 80C and 100C. In several experiments ferric sulfate and cupric sulfate were added in small amounts in order to study their inhibitor effects. See Table I for the experimental results.

Dissolving rates for zirconium metal in nitric acid-hydrofluoric acid mixtures were obtained at several temperatures. One dissolver solution tested contained 50 per cent nitric - 0.10 per cent hydrofluoric acid while the rest consisted 20 per cent - 3 per cent nitric-hydrofluoric acid mixtures. These data are summarized in Table II.

Corrosion experiments to establish initial rates were conducted with stainless steel types 302, 304, 316, 347 and Chlorimet 2 in sulfuric acid at 80C and 100C. Several of the dissolver solutions were saturated with ferric sulfate to observe inhibitor effects. These data are shown in Table III. Types 302, 304 and 347 can be eliminated immediately for use in 80 per cent sulfuric acid at 100C. Three day tests were next carried out on type 316 and Chlorimet 2 using 86 per cent sulfuric acid at 100C, the 316 was also studied as a function of the cupric or ferric sulfate concentration. See Table IV for these results.

Initial corrosion rates for various stainless steels in twenty per cent nitric acid - three per cent hydrofluoric acid at several different temperatures were established. Results for types 302, 304, 316, 321 and 347 are shown in Table V. As the more resistant types became available, four to five day tests were conducted in the same solution with 309, 309 Cb, Duri-met 20, 316 elc and 347. The experiments carried out at 57C were conducted in Tygon paint lined round bottom flasks while those at 30C were done in paraffin lined glass. In order to obtain data on welded samples, heliarc welded samples of the above types were produced and these samples also subjected to the "20-3" dissolver. See Table VI for these results.

Corrosion rates were expressed in mils penetration per year which were calculated from weight losses. This, then is an average penetration and does not account for localized deep penetrations. There was, on some samples, evidence for slight intergranular corrosion. On the whole, the corrosions were quite uniform. Corrosion rates of stainless steels determined in this mixture will undoubtedly be greater than observed in a dissolution of zirconium since the average free hydrofluoric acid concentration during a dissolution is smaller than three per cent.

TABLE I

DISSOLVING RATES OF ZIRCONIUM IN SULFURIC ACID		
Acid, %w	Temp. , C	Dissolution Rate mg/cm ² /hr
86	100	740 (a)
86	100	560 (b)
86	80	60
90	100	110
90	80	70
96	100	40
96	80	20

(a) Same rate with and without saturated ferric sulfate solutions.

(b) Saturated cupric sulfate solution.

TABLE II

DISSOLVING RATES OF ZIRCONIUM IN NITRIC ACID-HYDROFLUORIC ACID SOLUTIONS			
HNO ₃ , %w	HF, %w	Temp. , C	Dissolution Rate mg/cm ² /hr
50	0.10	Reflux	110
20	3.0	26	110
20	3.0	57 (a)	370
20	3.0	73 (a)	560

(a) A white precipitate occasionally formed.

TABLE III

INITIAL CORROSION RATES OF SOME STAINLESS STEELS IN SULFURIC ACID							
Acid %w	Temp., C	Exposure Timing hrs	Penetration, Mils/Year				Chlorimet 2
			302	304	316	347	
86	99	2.	-	1590 (a)	111 (a)	655 (a, b)	-
86	99	2.	-	-	1210 (b)	880 (b)	-
86	99	2.	-	-	1780	18600	-
86	80	2.	7600	3700	435	680	-
86	80	2.	-	-	160 (b)	290 (b)	-
86	80	2.	-	-	5 (a, b)	140 (a, b)	-
86	60	2.	290	185	-	-	-
86	60	2.	158 (b)	109 (b)	-	-	-
90	98	2.	-	3430	-	-	-
90	80	2.	-	2980	-	-	-
96	80	2.	134	153	-	-	-
86	225	3.	-	-	-	-	4760
86	225	3.	-	-	-	-	2070

(a) Sulfuric acid saturated with ferric sulfate.

(b) Initial surface passified with 85 per cent_w sulfuric acid at 100C for one hour.

TABLE IV

CORROSION RATES OF STAINLESS STEELS 316 AND CHLORIMET 2 IN 86% _w SULFURIC ACID				
Stainless Steel	Inhibitor % _w	Temp C	Immersion Time, hrs.	Penetration, Mils/Yr.
Chlorimet 2	-	96	66	1.4
Chlorimet 2	-	96	66	0.9
316	CuSO ₄ 2.2	99	65	56 (a)
316	CuSO ₄ 0.4	99	44	31 (a)
316	CuSO ₄ 0.14	99	44	30 (a)
316	Fe ₂ (SO ₄) ₃ 2.2	99	65	605 (a)
316	Fe ₂ (SO ₄) ₃ 0.4	99	44	820 (a)
316	Fe ₂ (SO ₄) ₃ 0.14	99	44	800 (a)

(a) Initial surface passified with 86 per cent _w sulfuric acid @ 100C for 1 hour.

TABLE V

INITIAL CORROSION RATES OF SOME STAINLESS STEELS IN NITRIC ACID - HYDROFLUORIC ACID SOLUTIONS								
HNO ₃ , % _w	HF, % _w	Temp., C	Exposure Time, hrs.	Penetration, Mils/Year				
				302	304	316	321	347
50	0.10	Reflux	1 1/2	-	770	600 (a)	-	-
20	3.0	26	2 1/2	430	460	180	180	250
20	3.0	57	1 3/4	530	520	360	400	390
20	3.0	73	1 1/4	-	-	420	460	-
20	3.0	111	1	-	-	1750	1680	-

(a) Surface passified with boiling 70 per cent HNO₃.

TABLE VI

THE CORROSION OF SOME STAINLESS STEELS IN 20% NITRIC ACID - 3% HYDROFLUORIC ACID						
Stainless Steel Type	Temp., C	Exposure, Time, hrs.	Penetration, Mils/Year			
			Total Immersion		50% Immersion	
			Non Welded	Welded	Non Welded	Welded
309	30	92.	70	-	54	-
309	57	114.	139	154	83	197
309 Cb	30	92.	62	25	37	26
Durimet 20	30	92.	19	-	14	29
Durimet 20	30	138.	19	-	15	-
Durimet 20	31	46	19	29	15	27
304 elc	57	114	-	800 (a)	1290	-
316 elc	57	114	-	590 (a)	810	-
347	57	114	270	312	191	190

(a) 309 Cb welds

DISCUSSION

When the data obtained for the dissolving rate of zirconium metal in sulfuric acid are added to the limited information in the literature, it is seen that a definite maximum corrosion rate occurs with 90 per cent _w sulfuric acid. The higher the temperature, the higher the rate of corrosion. The presence of such inhibitors as ferric sulfate or cupric sulfate had no noticeable effect on the corrosion rate.

An exhaustive study of the dissolution of zirconium in nitric-hydrofluoric acid mixtures has been reported in report LRL-73*.

Chlorimet 2 had the greatest resistance to 86 per cent sulfuric acid solution at 100C, the penetration being less than 2 mils/yr. Type 316 was also resistant under these conditions if 0.14 per cent cupric sulfate was added. Durimet 20 was not tested but an estimated value for this alloy would be a penetration of 60 - 100 mils/yr. It should be noted that the corrosion of the Chlorimet 2 at reflux temperature (225C) is too high to be satisfactory. If the zirconium cladding is to be removed at temperatures above 100C, more work on corrosion is needed.

* Gercke, R. H. J. and W. H. McVey, LRL-73, December, 1953.

Of the ten alloys tested in 20-3 solution only 309-Cb and Durimet 20 gave good corrosion resistance. Several of the alloys gave poor results because of excessive corrosion at the weld. If the temperature were to be raised to reflux temperature (110C) probably none of the alloys would be satisfactory and other materials such as Fluorothene-A would have to be used.

CONCLUSION

Zirconium metal can be readily dissolved in 90 per cent sulfuric acid at 100C or higher. Initial dissolution rates are high in a 20 per cent nitric - 3 per cent hydrofluoric acid mixture at above room temperatures.

Chlorimet 2 was found to have very good resistance to 86 per cent sulfuric acid at 100C but was unsatisfactory at 225C. Durimet 20 was estimated to be satisfactory at 100C. If the dissolution of zirconium is to be carried out at elevated temperatures, more work on corrosion in 90 per cent sulfuric acid will be needed.

Only 309-Cb and Durimet 20 gave good corrosion resistance to 20-3 solution at 30C. Fluorothene-A would probably be found to be satisfactory although more information is needed before definite recommendation can be made.