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AN EVALUATION OF THE SULFURIC ACID-SODIUM NITRITE ETCH FOR ZIRCALOY-2

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An Evaluation of the Sulfuric Acid-Sodium Nitrite Etch for Zircaloy-2

INTRODUCTION

A subcontract for the development of an etch for zirconium and zirconium-tin alloys was placed with Manufacturing Laboratories, Inc.[1] An etch is necessary to remove distorted surface metal and contaminants embedded in the surface by machining. The etch should not be harmful to corrosion resistance, should remove up to four mils per surface in a reasonable time, should produce a clean surface with no pitting, and should be easy to prepare and handle.

The present etch, which consists of 450 ml 70% nitric acid, 50 ml 48% hydrofluoric acid, and 500 ml water, does not meet all the above specifications. It is difficult to handle as it must be stored in polyethylene tanks and hydrofluoric acid safety precautions must be strictly observed. If any acid remains on the metal surface, impaired corrosion resistance results. Furthermore, the material to be etched must be vigorously agitated or channeling will occur, and the bath must be maintained at 100 $\pm$ 10°F. When material is etched according to the specified procedure[2], one mil per minute is removed, and the bath is spent after approximately 56 grams of metal are dissolved per liter of solution. The surface produced is bright and smooth.

The results of work done on the subcontract are presented in the progress reports of Manufacturing Laboratories, Inc.,[3,4,5,6 7,8] and are to be summarized in a final report. A 'shot-gun' technique was first employed for screening many chemical reagents for etching ability. A promising etch, consisting of 96.2% sulfuric acid to which is added 120 grams sodium nitrite per liter of acid, was finally developed. This solution is easier to handle than the present etch and the safety hazard of hydrofluoric acid is eliminated. The temperature of the bath should be maintained below 105°F for optimum performance.

Specimen agitation is not necessary; however, bath agitation is recommended. With the solution maintained at 95°F and agitated, 0.34 mil per minute is initially removed; and the bath is exhausted after approximately 20 grams of metal are dissolved per liter of solution. The surface produced is not quite as bright as that obtained using the present nitric-hydrofluoric etch, nor is the microstructure as clearly visible.

Three serious drawbacks to the etch are that sulfur floats to the surface of the solution, a white precipitate forms upon cooling, and the specimens darken upon removal from the solution if they are not immediately rinsed in water. However, the latter effect can be minimized since the lower the temperature of the bath when the specimen is removed, the longer the time permissible before rinsing in water.

PRESENT EXPERIMENTS

The present experiments were designed to:

(1) Investigate the effect of the sulfuric-nitrite etch upon the corrosion resistance of Zircaloy-2 and to compare the corrosion rates of specimens etched by the sulfuric-nitrite solution and the nitric-hydrofluoric acid solution.

(2) Investigate the effect of residual etchant from both solutions upon the corrosion resistance of Zircaloy-2.

1. Effect of Etch Upon Corrosion Resistance

Samples of Zircaloy-2, 1" x 1/2" x 1/8" were etched in the prescribed manner with the sulfuric-nitrite solution and with the nitric-hydrofluoric acid solution long enough to remove two mils per side. After weighing, the specimens were submitted to corrosion test at 680°F in a degassed, demineralized water.

The data, shown in Figure 1 and Table I, indicate that the sulfuric-nitrite etch has no harmful effect upon the corrosion resistance of Zircaloy-2.

The surface appearances of the specimens etched with the sulfuric-nitrite solution were not as black as those etched with the nitric-hydrofluoric acid-solution. However adherent, lustrous oxide films were produced. The specimens are shown in Figure 2.

2. Effect of Residual Etchant Upon Corrosion Resistance

Samples of Zircaloy-2 were etched with the sulfuric-nitrite solution and with the nitric-hydrofluoric acid solution long enough to remove two mils per side. The etching solution was permitted to drain off, but no rinsing was performed. After the specimens were dried, they were corrosion tested at 680°F in degassed, demineralized water.

The specimens, as shown in Figure 3, were covered with white oxide films. The films present on the samples etched with the sulfuric-nitrite solution appeared to be somewhat more adherent than those on the specimens etched with the nitric-hydrofluoric acid solution.

The data, shown in Table I and Figure 1, indicate that although the residual etchants from both solutions have a deleterious effect upon the corrosion resistance of Zircaloy-2, the weight losses of the unwashed sulfuric-nitrite etched specimens were much less than those of the unwashed nitric-hydrofluoric etched specimens.

Additional samples of Zircaloy-2 were handled as above except that the specimens were vigorously scrubbed with a brush under water after drying. The specimens, as shown in Figure 4, were again coated with white oxide films after corrosion testing.

Reference to Figure 1 and Table I shows that the corrosion resistance of specimens which were scrubbed after allowing the etchant to dry is improved over that of the unscrubbed specimens. While the weight gains for the scrubbed specimens compares favorably with those of the properly etched and washed specimens, their appearance indicates that all of the residual etchant was not removed. The improvement of corrosion resistance due to scrubbing is more pronounced in the case of sulfuric-nitrite etch than in the case of the nitric-hydrofluoric etch.

GENERAL DISCUSSION

The nitric-~~hydrofluoric acid~~ etch is superior as a pickling solution for zirconium to the sulfuric-nitrite etch, as developed by Manufacturing Laboratories Inc., even though it is more difficult to handle, contains hazardous hydrofluoric acid, and the residual etchant has been shown to have a very deleterious effect upon the corrosion resistance. However, a development program proposed by Rothman[9] may lead to modification of the sulfuric-nitrite etch to overcome the low rate of attack, low bath life, and precipitate formation.

A tabular comparison of the two etching solutions is shown below:

Characteristic	HNO_3-HF	H_2SO_4-$NaNO_2$
Etching -		
Rate	1 mil/min	0.34 mil/min
Finish	Satisfactory	Satisfactory
Tendency for sample to discolor		Greater
Residual etchant	Very deleterious	Deleterious
Bath -		
Life	56 g/l	20 g/l
Rejuvenation	Yes, but not advisable	Not known
Temperature Limits	$100 \pm 10^{\circ}F$ *	$95 \pm 10^{\circ}F$ **
Handling		Easier
Cost		Less

* specified limits, conservative
** actual limits, would have to be narrowed for large scale practice

Conclusions

Preliminary experiments indicate that there are no significant differences in the corrosion rates of zirconium or Zircaloy-2 after etching with the nitric-hydrofluoric solution or the sulfuric-nitrite solution, provided proper etching and washing techniques are followed. Incomplete removal of the residual etchant is deleterious to the corrosion resistance; however, this effect in the case of the sulfuric-nitrite solution is not as pronounced as in the case of the nitric-hydrofluoric acid solution.

The anticipated advantages in the new etch were not completely realized. Additional development aimed at modifying the sulfuric-nitrite etch would have to be performed in order to overcome the disadvantages before recommendation for the adoption of the etch could be made.

Prior to this investigation, it had been supposed that impaired corrosion resistance of improperly washed specimens was due to fluorides alone. It has now been shown that sulfates and/or nitrites will also exhibit this effect.

REFERENCES

1. Subcontract Number 14-333 with Manufacturing Laboratories, Inc. 272 Northampton Street, Boston 18, Mass.

Delete 2. ~~Specifications for Cleaning and Pickling Fuel Plates, Sub Assemblies and Clusters. WAPD-C-60 - P. Cohen - 2/20/52~~

3. Progress Report, Manufacturing Laboratories, Inc. - 2/1/53

4. " " " " " - 3/2/53

5. " " " " " - 4/8/53

6. " " " " " - 6/1/53

7. " " " " " - 7/1/53

8. " " " " " - 8/1/53

9. A. B. Rothman, "Non-HF Etchs Developed by the Manufacturing Laboratories", WAPD-MM-247, August 8, 1953.

TABLE I

Etching Solution	Condition	No. Samples	Time, days	Weight Change mg/dm^2	Appearance
HNO_3-HF	Properly washed	4	14	+ 19.3	Black
			28	+ 23.8	"
			42	+ 24.3	"
			56	+ 28.5	"
H_2SO_4-$NaNO_2$	Properly washed	9	14	+ 15.4	Black
			28	+ 20.5	"
			42	+ 22.9	"
			56	+ 27.8	"
			70	+ 29.2	Dark gray
HNO_3-HF	Dried	5	14	- 245	Marbled
			28	- 290	"
			58	- 338	"
H_2SO_4-$NaNO_2$	Dried	5	14	- 166	Marbled
			28	- 165	"
HNO_3-HF	Dried-Scrubbed	5	14	- 44.5	Marbled
			28	- 57.2	"
			58	- 61.0	"
H_2SO_4-$NaNO_2$	Dried-Scrubbed	5	14	+ 26.0	Marbled
			28	+ 22.8	"
			58	+ 23.6	"

WEIGHT CHANGE vs TIME AT 680° F

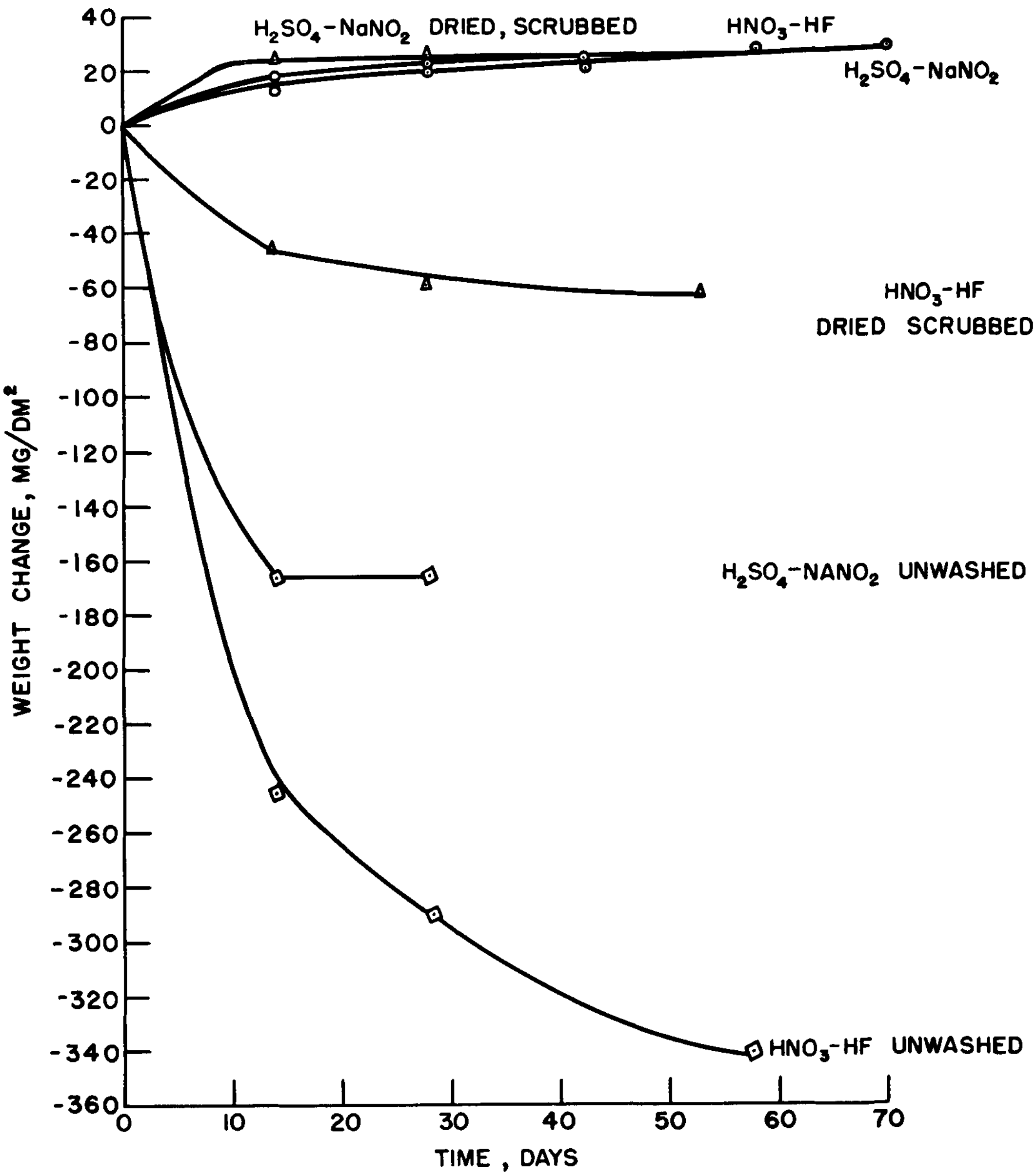
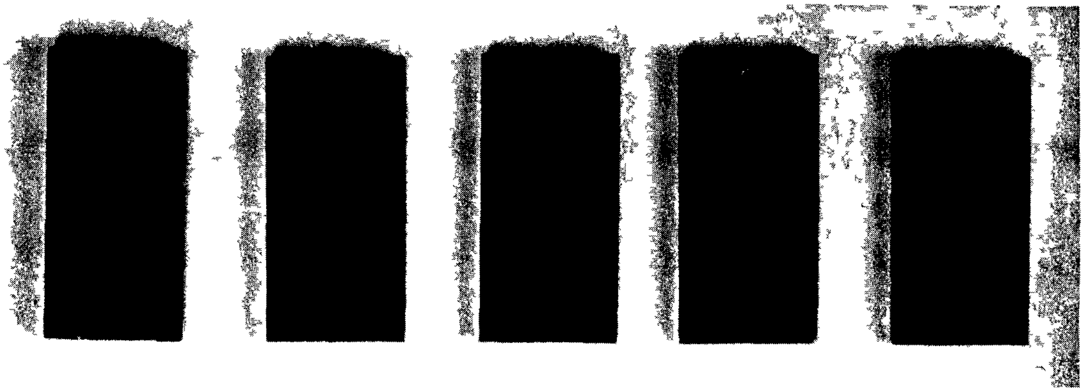


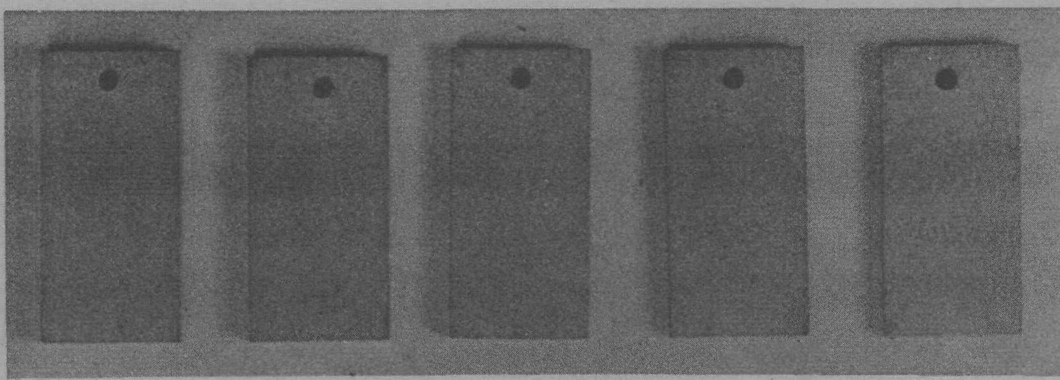
FIG. 1



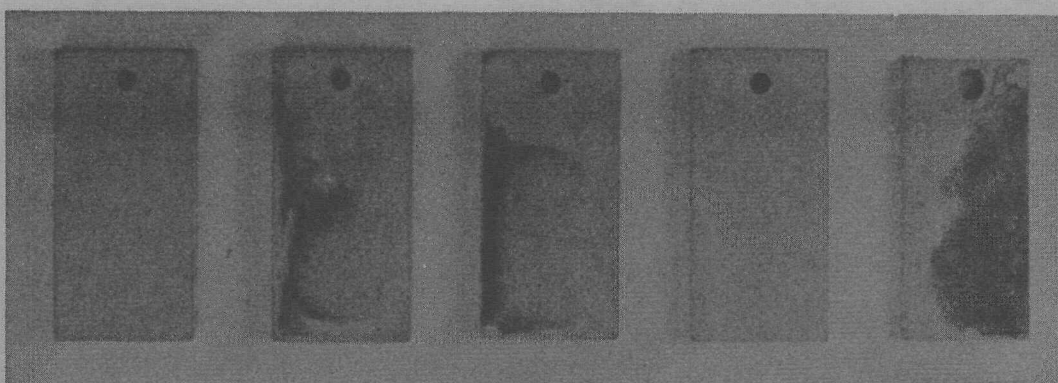
Etched in the nitric-hydrofluoric acid solution, rinsed and washed. Corrosion tested for 42 days in 680°F water.

Etched in the sulfuric-nitrite solution, rinsed and washed. Corrosion tested for 42 days in 680°F water.

Figure 2



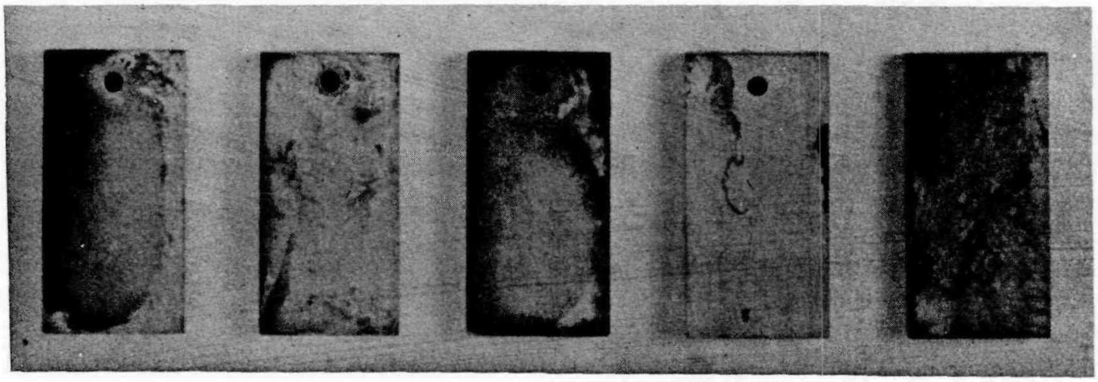
Etched in the nitric-hydrofluoric acid solution, without any rinsing or washing. Corrosion tested for 58 days in 680°F water.



Etched in the sulfuric-nitrite solution, without any rinsing or washing. Corrosion tested for 28 days in 680°F water.

Figure 3

Etched in the nitric-hydrofluoric acid solution and allowed to dry, then vigorously scrubbed with a brush. Corrosion tested for 58 days in 680°F water.



Etched in the sulfuric-nitrite solution and allowed to dry, then vigorously scrubbed with a brush. Corrosion tested for 58 days in 680°F water.

Figure 4