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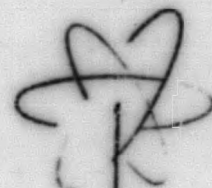
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MASTER

# SPECIFIC ZIRCONIUM ALLOY DESIGN PROGRAM

## QUARTERLY PROGRESS REPORT NO. 7

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SAN JOSE, CALIFORNIA



EURAEC  
GEAP-4484  
Joint US-EURATOM  
Research and Development  
Program

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Quarterly Progress Report No. 7

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January 1964

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**FOREWORD**

"The United States and the European Atomic Energy Community (EURATOM), on May 27, 1958 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint US-EURATOM research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

"The work described in this report represents the Joint US-EURATOM effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in western Europe and United States."



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SUMMARY

All experimental work under the Corrosion Mechanism task has been completed. The remaining topical reports are being prepared by D. L. Douglass, now on assignment at Mol.

Experimental work on the first round of 31 alloys and on the second round of 10 alloys has been completed. Steam exposures of at least 3000 hours were finished for all alloys at all test temperatures, with exposures of some coupons to 6700 hours. Mathematical expressions have been derived to describe all first round data for corrosion rates and hydriding rates at 300, 400, and 500°C as a function of Nb, Cr, Fe, and Cu content. Solution of the equations for particular service temperatures yield Zr-Cr alloys as optimum at lower temperatures and Zr-Cu-Fe alloys as optimum at the higher temperatures. The second round test results show that neither Ni nor Be additions to Zr-Cr or Zr-Cu improve the performance over that of the optimum Zr-Cr or Zr-Cu-Fe alloys.

For the first round heat treatment used, post-corrosion ductility depends on two factors in addition to alloy composition and hydrogen content: crystallographic texture and intermetallic aging reactions. Alloys with a high original ductility are embrittled less by a given amount of hydrogen than are alloys with low original ductility. From the second round tests, it was found that raising the final alpha annealing temperature from 565 to 788°C gives better over-all corrosion, hydriding performance, and resistance to hydrogen embrittlement for both the Zr-Cr and Zr-Cu alloys tested.



This is the seventh quarterly progress report under a program initiated January 29, 1962 under Contract AT(04-3)-189, Project Agreement 24.

Under the Specific Zirconium Alloy Design Program, we are investigating the design of a zirconium-base alloy for application as nuclear fuel cladding for steam service. Both a basic mechanistic approach (Task A) and a statistically designed empirical approach (Task B) are included in the program.

Two topical reports<sup>1,2</sup> and the previous quarterly reports<sup>3-8</sup> have presented the results of the Task A, corrosion mechanism work. The present status of Task A work is given in Section I.

The results of the Task B, alloy design, study have been reported in three topical reports<sup>9-11</sup> and in the previous quarterly reports.<sup>3-8</sup> The present status of this task is also given in Section I and the technical findings of the last quarter are reported in Section III.



## I. PROGRAM STATUS

A brief summary of the present status of the program is presented.

### TASK A - CORROSION AND HYDROGEN PICKUP MECHANISM STUDIES

A method was developed for stripping corrosion films; these films were subjected to analyses by wet chemistry, microprobe, radiochemical, and neutron activation methods.<sup>7</sup> Except for issuing the final topical report, this work is complete.

Hydrogen overvoltage and electrode potential measurements on zirconium intermetallic compounds have been completed and reported.<sup>2</sup>

Oxygen diffusion kinetics for non-stoichiometric zirconium oxide have been determined and reported.<sup>1</sup> Oxygen diffusion in zirconium oxide doped with Al, Ni, Y, Cr, and Fe has been measured and a final topical report is in preparation by D. L. Douglass.

### TASK B - ALLOY DESIGN FOR STEAM SERVICE

Target properties for the design were chosen and the alloy field for study was selected, as reported in May 1962.<sup>3</sup>

The fabrication of 32 alloys statistically chosen from the alloy field for evaluation, the preparation of test coupons, and the chemical analyses of all alloys has been completed. A topical report of this work was issued in December 1962.<sup>4</sup>

All experimental alloys were tested, as-fabricated, in impact tests and in tensile tests and the results reported.<sup>5</sup>

Corrosion testing in refreshed steam loops<sup>10</sup> was initiated and the first examination was completed September 1962. The target exposure of 3000 hours was exceeded at the three test temperatures, 300, 400, and 500°C,



in May 1963. Extra coupons of selected alloys were continued at 500°C and terminated in November 1963 after 6792 hours; extra coupons of all alloys are being continued at 300°C (now beyond 8000 hours).

Impact testing of all samples after corrosion exposures up to and exceeding the target exposures has been completed. Post-corrosion tensile tests are complete for all coupons exposed for tensile test temperatures of room temperature, 300 and 500°C; tensile tests at 400°C were canceled. All hydrogen analyses of all coupons exposed at each test temperature are complete.

Computation of test results and a statistical analysis<sup>11</sup> of preliminary data began November 1962. The final analysis of the weight gain data for all exposures is complete. Final analysis of the hydrogen pickup data is 90% complete. Embrittlement studies are complete.

A second round of evaluation of 10 additional alloys was initiated in March 1963. This evaluation is now complete and the results are reported.



**II. TASK A - CORROSION MECHANISM STUDIES - TECHNICAL PROGRESS**

All experimental work was completed by November 15, 1963. The scientist conducting the work, D. L. Douglass, left for an assignment at Mol at that time. Final topical reports are being prepared.



### III. TASK B - ALLOY DESIGN - TECHNICAL PROGRESS

Two rounds of alloy evaluation have been completed. The first round included 31 zirconium-base alloys chosen by statistical design from a field which included 0 to 4.0 at. % Nb; 1.0 to 2.6 at. % Cr; 0.7 to 2.2 at. % Cu; and 0.37 to 0.55 at. % Fe. The first round evaluation was to determine the compositional dependence of corrosion rate, hydriding rate, and resistance to hydrogen embrittlement during exposure to high-pressure, refreshed steam at 300, 400, and 500°C. The second round objectives were (1) to explore the effect of minor additions of Ni or Be to the better alloys, Zr-Cr and Zr-Cu, and (2) to determine the effect of three alternate fabrication schedules on the performance of two of the better alloys selected as the result of an interim analysis of the first round data.

#### FIRST-ROUND RESULTS

In the last quarterly report,<sup>8</sup> the effect of compositional variation on the combined corrosion and hydriding performance was reported for the Zr-Cu, Zr-Cu-Fe, and Zr-Cr-Fe alloys over the entire temperature range of 300 to 500°C. The analysis reported was based on data for exposures up to approximately 3500 hours. Data for some alloys up to 6792 hours are now available for 500°C exposures and up to 6570 hours for all alloys exposed at 300°C. The predictions for corrosion and hydriding rates based on the 3500-hour data have been compared to the new, longer-term results. Further data on post-corrosion mechanical behavior are also available.

Topical reports on the corrosion facilities<sup>10</sup> and the statistical methods<sup>11</sup> used in the Specific Alloy Design Program were issued this quarter. The method of hydrogen analysis employed in the program is described in Appendix A; the methods of chemical analyses for alloy content appear in Appendix B.



### Corrosion and Hydriding Rates

Although 3000 hours was the target exposure for round one alloys, a few specimens were left in the 300 and 500°C autoclaves until almost a 7000-hour exposure was reached. The coupons were removed and weighed at several time points beyond 3000 hours to obtain valuable information about the dependence of corrosion rate on time.

Data resulting from the extended exposures have not yet been analyzed in detail. No analysis has been made of the 300°C data. Attention has been directed thus far at the 500°C weight gain data, with an additional rough analysis having been made of the 500°C hydriding data. Results of these two analyses are presented.

#### 500°C Corrosion Rate

It was assumed in previous work that steady state was reached by a 750-hour exposure. The corrosion rate for a given coupon was then found by observing the rate of weight gain in the interval from 750 to 3000 hours. With data now extending an additional 3800 hours, it was possible to determine if steady state had truly been reached by 750 hours, as it appeared from the earlier data.

The specimens which remained in the 500°C autoclave until almost 7000 hours were removed and weighed at 75, 175, 375, 750, 1125, 1500, 3000, 3792, 4542, 4917, 5667, and 6792 hours. There were two such specimens for each of the 14 better performing alloys. To determine when steady state was reached, the corrosion rate was estimated for each time interval for each of the specimens. For example, the corrosion rate in the 375- to 750-hour interval was found by subtracting the weight at 375 from that at 750, finding the weight gain per unit area, and dividing by the exposure time. Results are given in Table 1.

The data in Table 1 were analyzed after being converted to natural logarithms to stabilize the variance. It was found that samples 33 to 59



TABLE 1. Incremental Corrosion Rates, mg/dm<sup>2</sup>/day (500°C)

Alloy	Sample	Time Interval (Hours of Exposure)											
		0-75	75-175	175-375	375-750	750-1125	1125-1500	1500-3000	3000-3792	3792-4542	4542-4917	4917-5667	5667-6792
1	33	16.5	6.51	6.82	6.06	4.40	4.07	5.80	3.94	4.02	4.32	3.68	3.64
	59	18.6	6.37	6.21	6.08	4.58	4.52	5.02	3.58	3.64	4.73	4.02	4.15
5	33	19.0	6.20	6.98	3.57	2.49	3.40	4.10	1.79	1.48	1.66	2.35	1.93
	59	23.5	7.53	6.31	4.21	1.77	2.60	3.43	2.30	1.92	1.92	3.12	2.58
13	33	14.1	2.17	4.19	5.81	2.99	3.24	3.80	2.81	1.56	3.74	1.78	2.35
	59	16.0	3.47	4.37	4.89	3.12	3.74	3.67	2.16	2.03	2.50	2.61	2.36
14	33	24.8	12.40	11.16	7.39	3.82	6.14	5.33	5.15	3.40	3.40	3.63	3.12
	59	25.8	8.11	7.57	4.68	2.70	2.76	4.72	3.79	2.81	3.64	4.08	3.08
17	33	14.1	4.34	2.48	3.98	3.57	2.32	3.44	2.57	1.89	2.91	1.53	2.18
	59	18.6	3.47	2.91	2.18	2.70	2.03	2.39	0.94	3.12	0.68	3.02	1.62
18	33	14.1	4.03	2.48	1.74	5.48	2.99	2.67	2.03	1.93	1.99	1.53	1.85
	59	16.5	3.09	2.52	1.82	2.08	2.81	2.59	2.33	1.51	2.91	1.29	2.18
19	33	18.2	4.03	3.26	1.83	1.58	2.99	3.95	2.89	2.01	3.57	2.60	2.29
	59	17.5	4.05	3.98	3.64	4.26	5.25	4.30	2.90	2.31	4.99	2.48	2.58
20	33	22.3	7.75	8.06	6.89	5.31	3.40	5.38	4.88	3.49	3.40	2.97	3.34
	59	22.2	7.72	7.08	5.67	4.06	4.99	4.50	3.55	3.22	2.81	3.59	3.61
24	33	17.8	4.96	4.34	4.23	4.57	4.65	4.87	3.00	2.99	4.15	2.85	2.46
	59	17.0	4.44	3.01	2.18	2.86	3.74	3.65	2.33	1.95	4.84	2.04	1.75
26	33	36.0	3.41	3.41	2.24	2.57	1.16	2.52	1.09	2.58	0.75	0.91	1.74
	59	33.0	4.63	2.72	1.98	1.61	2.03	2.09	0.84	1.82	1.98	1.19	1.96
27	33	16.9	10.23	13.80	10.38	7.14	7.39	8.61	6.47	5.45	5.15	4.91	3.73
	59	25.0	6.95	9.99	7.54	6.45	6.40	7.28	5.81	4.97	4.84	6.22	5.25
28	33	12.4	5.27	8.99	6.23	4.98	4.57	5.42	3.47	3.44	4.15	3.10	2.87
	59	15.2	5.98	9.22	6.55	4.99	4.42	4.68	2.62	2.65	3.90	3.02	2.70
29	33	13.6	4.34	4.96	6.56	4.07	3.74	3.60	4.84	2.83	5.31	3.01	3.31
	59	17.5	5.02	4.17	4.52	4.21	4.37	4.55	3.67	2.44	5.88	3.17	3.70
30	33	17.8	4.96	4.74	6.23	4.32	4.15	4.60	3.94	3.12	3.65	2.93	3.28
	59	13.9	5.21	4.37	5.56	4.00	4.06	3.95	2.90	2.00	4.63	2.45	3.08

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(the tensile and the impact specimens) were not unlike in their behavior. A small, but statistically significant, interaction between alloy and exposure time was found which indicated that the relationship between corrosion rate and time is not the same for all alloys. Some alloys appear to reach steady state before others, although this is not a strongly significant result and is more a difference in degree, rather than in kind, of behavior. A more detailed look at the time-corrosion rate relationship is warranted.

Since the interaction is small, average corrosion rates over time are meaningful. These corrosion rates are given below for the 14 alloys.

TABLE 2. Average Corrosion Rates for Different Exposure Intervals

<u>End of Time Interval, h</u>	<u>Natural Logarithm Rate, av</u>	<u>Antilogarithm, mdd</u>
75	2.921	18.6
175	1.652	5.22
375	1.634	5.13
750	1.462	4.32
1125	1.269	3.56
1500	1.284	3.61
3000	1.423	4.15
3792	1.053	2.87
4542	0.950	2.59
4917	1.149	3.16
5667	0.970	2.64
6792	0.987	2.68

From this table, it is clear why experience through 3000 hours had made the assumption of steady state by 750 hours reasonable. Based on the rates observed in the preceding and succeeding intervals, the corrosion rate in the interval from 1500 to 3000 hours was higher than it should have been. This was a consistent result, as reference to Table 1 shows. No explanation for this is offered at this time.

The data of Table 1 indicate that steady state is not reached until at least 3000 hours. Corrosion rates were estimated for each of the



specimens from 3000 to 6792 hours. These rates compared with estimates for the 750- to 3000-hour interval. The comparisons are shown in Table 3.

TABLE 3. Comparisons of Corrosion Rate Estimates, mdd

Alloy	Sample	Hours of Exposure Estimated Rate	
		750-3000	3000-6792
1	33	5.21	3.86
	59	4.82	3.96
5	33	3.66	1.87
	59	2.99	2.44
13	33	3.53	2.31
	59	3.56	2.32
14	33	5.15	3.73
	59	4.02	3.43
17	33	3.24	2.15
	59	2.36	1.95
18	33	3.15	1.85
	59	2.52	1.98
19	33	3.35	2.55
	59	4.42	2.28
20	33	4.97	3.63
	59	4.47	3.44
24	33	4.73	2.92
	59	3.51	2.27
26	33	2.27	1.51
	59	1.99	1.55
27	33	8.06	5.02
	59	6.94	5.47
28	33	5.14	3.28
	59	4.65	2.86
29	33	4.31	3.68
	59	4.43	3.56
30	33	4.42	3.36
	59	3.95	2.86

An analysis of the data in Table 3, again using logarithms, yielded the very important result that the bias associated with the earlier estimates



of the corrosion rate was the same for all alloys. This bias is estimated to be 29%, i.e., the steady-state rate, assumed to begin at 3000 hours, is 71% of the rate based on the 750- to 3000-hour interval. By assuming that the same is true for the 17 alloys not exposed beyond 3000 hours, leads to conclusion that the response surface estimated previously is unchanged except for being decreased by 29% at all points on the surface. Thus, the optimum regions occur at the same alloy combinations, but the estimated rates in these regions are lower than reported previously.

#### 500°C Hydriding Rate

In estimating hydriding rates, only the 1125- and 3000-hour data were used previously for the 14 alloys that receive extended exposures. Data taken before 750 hours were excluded because steady state was not reached before 750 hours. The 750- and 1500-hour data points were suspect because the samples analyzed experienced weight gains quite different from the other samples, which indicated that they must have been subjected to a somewhat different test environment. Thus, the extended exposure data were quite valuable in providing better estimates of the hydriding rate.

Depending on the alloy, samples were measured for hydrogen content at varying exposures, either at 3792, 4542, 4917, or 6792 hours. Eight of the 14 alloys had two additional time points beyond 3000 hours, while the remaining six had one time point. Hydriding rate estimates are shown in Table 4, and are compared with those used in the estimation of the response surfaces.

TABLE 4. Hydriding Rates, ppm/day

<u>Alloy</u>	<u>1125-3000 h</u>	<u>Over-All Rate</u>
1	4.77	4.66
5	2.23	1.16
13	3.15	1.63
14	1.32	2.16
17	1.66	2.93
18	3.66	2.17
19	2.41	1.60
20	2.37	2.72
24	4.38	3.16
26	2.57	3.49
27	4.79	4.80
28	3.57	3.63
29	2.76	2.78
30	3.42	3.82



It is seen that these estimates differ considerably for some alloys. The difference is attributed to sampling variation; the standard deviation associated with each estimate in Column 1 of Table 4 is about 1.2 ppm/day, while in Column 2 it is between 0.4 and 0.7 ppm/day, depending on the alloy. Thus the large discrepancies are not surprising.

No significant bias was found between the two sets of estimates. Although this means that the existing response surface is unbiased, it should be re-estimated by using the revised hydriding rate estimates because they have much smaller uncertainties associated with them. This will result in a better estimate of the response surface relating hydriding rate to alloy content.

#### Post-Corrosion Mechanical Properties

Tensile and impact tests after the longest corrosion exposures continue to show evidence of a recovery in loss of ductility for certain alloys. This observation is consistent with metallographic results which show that intermetallic phases are responsible for an aging and over-aging reaction in the more complex compositions.

A summary of the alloys found to be completely embrittled in room temperature tensile tests as a function of exposure time at 500°C is shown below.

<u>Exposure Time at 500°C</u>	<u>Number Brittle Alloys RT Tensile Tests (<math>\leq</math> 10% RA)</u>
0	0
1125	6
1500	8
3000	13
3792	17
4542	18
4917	19
6792	20

Twelve alloys are not expected to be brittle even after 6792 hours at 500°C. Of these, the Cu, Cu-Fe, and Cr-Fe alloys (014, 017, 019, 024, 026) appear to have the greatest resistance to hydrogen embrittlement. Alloy 032, Zircaloy-2, became completely brittle between 3000 and 3792 hours at 500°C. The data taken so far show that the better first round alloys might reach 10,000 to 15,000 hours at 500°C before becoming brittle in room temperature tensile tests. No evidence has been found of brittle tensile behavior at 300°C and above.



## SECOND ROUND RESULTS

The second round experiments are now complete. Therefore, the interim data (1125 hours) and discussion reported in the last quarterly report will be expanded with the addition of all of the data out to the target exposures of 3000 hours.

### Nickel and Beryllium Additions

The first objective of the second round of evaluations was to see if minor additions of Ni or Be to Zr + 1.9 at. % Cr or to 1.2 at. % Cu lead to improved performance. The total corrosion exposure was 3000 hours at 300 and 500°C in steam. The final data are presented in Tables 5 through 8. The first round data on the effect of Fe additions are included in the tables.

At the levels tested, none of the minor additions (Fe, Ni, or Be) to Zr-Cr are beneficial at both 300 and 500°C in improving both corrosion resistance and hydrogen pickup. Nickel additions give high hydrogen at 300°C; beryllium additions give high hydrogen at 500°C. Iron is the best of the three, but is not beneficial to corrosion resistance at 500°C. For particular temperatures, there were alloys better than the Zr-Cr binaries. The Zr + 0.8 at. % Be alloy is very interesting at 300°C; the addition of 0.1 to 0.4 at. % Ni gives alloys which perform best at 500°C.

None of the Zr-Cu base alloys are better than Zircaloy-2 at 300°C. Iron is the best addition for 300°C service. At 500°C, all of the Zr-Cu alloys are good. Nickel is the best addition at 500°C; beryllium is the worst. Zr-Cu-Fe alloys show the best performance at both 300 and 500°C.

In comparing the Zr-Cu-Fe alloys with the Zr-Cr binaries, it is apparent that Zr-Cu-Fe would be preferred at higher service temperatures; Zr-Cr would be preferred at lower service temperatures. [Unfortunately, the simultaneous addition of Zr and Cu leads to a performance less desirable than for either addition alone.<sup>6</sup>]



TABLE 5. Steam Corrosion Weight Gain Data for Zr-Cr Base Alloys  
(Weight Gain, mg/dm<sup>2</sup>)

300°C Exposure

Alloy Addition (at. %)*	175 h	750 h	1125 h	1875 h	2250 h	3000 h
2.3 Cr	-	13.8	15.0	-	16.9	19.3
1.9 Cr	-	12.9	13.2	-	15.9	18.5
1.5 Cr + 0.2 Fe*	-	9.6	12.6	-	17.1	16.7
1.3 Cr + 0.5 Fe*	-	10.4	11.8	-	18.5	19.1
1.9 Cr + 0.1 Ni	-	12.9	13.4	-	15.3	17.5
1.9 Cr + 0.4 Ni	-	12.5	12.9	-	15.1	17.5
1.9 Cr + 0.4 Be	-	12.6	13.2	-	14.7	16.7
1.9 Cr + 0.8 Be	-	11.8	12.1	-	13.7	15.3
Zr-2*	-	12.3	14.0	-	17.1	18.3

(2σ limit ≈ ± 0.6 for each coupon group average)

500°C Exposure

2.3 Cr	51	123	188	313	-	439
1.9 Cr	56	131	198	303	-	423
1.5 Cr + 0.2 Fe*	72	134	183	-	-	456
1.3 Cr + 0.5 Fe*	68	161	228	-	-	564
1.9 Cr + 0.1 Ni	51	102	122	187	-	290
1.9 Cr + 0.4 Ni	53	102	124	180	-	301
1.9 Cr + 0.4 Be	44	132	181	287	-	407
1.9 Cr + 0.8 Be	41	89	123	228	-	345
Zr-2*	128	324	411	-	-	1115

(2σ ≈ ± 2) (2σ ≈ ± 4) (2σ ≈ ± 7) (2σ ≈ ± 7) (2σ ≈ ± 9)

\* Sponge Zirconium contained 0.05 at. % Fe.  
\*\* First Round data. All alloys fabricated  
by the same schedule: Beta treated, 565°C  
alpha anneal.



TABLE 6. Steam Corrosion Weight Gain Data for Zr-Cu Base Alloys  
(Weight Gain, mg/dm<sup>2</sup>)

<u>300°C Exposure</u>						
Alloy Addition (at. %)	175 h	750 h	1125 h	1875 h	2250 h	3000 h
1.2 Cu + 0.05 Fe	-	17.4	18.3	-	-	-
1.6 Cu + 0.2 Fe	-	17.1	17.3	-	20.1	22.5
1.2 Cu + 0.05 Fe*	-	15.7	18.8	-	19.1	20.0
1.1 Cu + 0.3 Fe*	-	11.6	13.2	-	25.4	26.9
1.2 Cu + 0.4 Ni + 0.2 Fe	-	18.8	19.7	-	17.1	18.5
1.2 Cu + 0.4 Be + 0.2 Fe	-	16.3	16.9	-	20.9	22.6
Zr-2*	-	12.3	14.0	-	17.7	20.1
					17.1	18.3

(2σ ≈ ± 0.6)

<u>500°C Exposure</u>						
Alloy	175 h	750 h	1125 h	1875 h	2250 h	3000 h
1.2 Cu + 0.05 Fe	86	195	213	257	-	323
1.6 Cu + 0.2 Fe	72	123	151	210	-	338
1.2 Cu + 0.05 Fe*	125	187	214	-	-	360
1.1 Cu + 0.3 Fe*	67	130	169	-	-	344
1.2 Cu + 0.4 Ni + 0.2 Fe	62	110	128	167	-	223
1.2 Cu + 0.4 Be + 0.2 Fe	50	118	158	265	-	395
Zr-2*	128	324	411	-	-	1115

(2σ ≈ ± 2) (2σ ≈ ± 4) (2σ ≈ ± 7) (2σ ≈ ± 7)

(2σ ≈ ± 9)

\* First Round data. All alloys fabricated by the same schedule: Beta treated, 565°C alpha anneal.



TABLE 7. Corrosion Hydrogen Data for Zr-Cr Base Alloys

<u>300°C Exposure</u>		Hydrogen Content (ppm)				
Alloy Addition (at. %)	0	750 h	1125 h	2250 h	3000 h	
2.3 Cr	11	-	16	21	21	
1.9 Cr	12	-	24	28	29	
1.5 Cr + 0.2 Fe*	(13)	-	-	30	32	
1.3 Cr + 0.5 Fe*	(13)	-	-	27	26	
1.9 Cr + 0.1 Ni	14	-	43	41	36	
1.9 Cr + 0.4 Ni	10	-	40	39	37	
1.9 Cr + 0.4 Be	9	-	34	33	28	
1.9 Cr + 0.8 Be	12	-	16	16	15	
Zr-2*	(13)	-	-	31	28	
<u>500°C Exposure</u>						
2.3 Cr	11	150	251	-	961	
1.9 Cr	12	90	133	-	663	
1.5 Cr + 0.2 Fe*	(13)	-	128	-	470	
1.3 Cr + 0.5 Fe*	(13)	-	162	-	351	
1.9 Cr + 0.1 Ni	14	72	70	-	384	
1.9 Cr + 0.4 Ni	10	72	80	-	388	
1.9 Cr + 0.4 Be	9	208	334	-	1004	
1.9 Cr + 0.08 Be	12	121	180	-	805	
Zr-2*	(13)	-	591	-	1563	

\* Sponge Zirconium contained 0.05 at. % Fe.

\*\* First Round data. All alloys fabricated by same schedule: Beta treated, 565°C alpha anneal.



TABLE 8. Corrosion Hydrogen Data for Zr-Cu Base Alloys

<u>300°C Exposure</u>		<u>Hydrogen Content (ppm)</u>				
<u>Alloy</u>	<u>Addition (at. %)</u>	<u>0</u>	<u>750 h</u>	<u>1125 h</u>	<u>2250 h</u>	<u>3000 h</u>
1.2 Cu + 0.05 Fe		14	-	67	64	65
1.6 Cu + 0.2 Fe		19	-	64	49	46
1.2 Cu + 0.05 Fe*		(13)	-	-	63	60
1.1 Cu + 0.3 Fe*		(13)	-	-	28	32
1.2 Cu + 0.4 Ni + 0.2 Fe		8	-	35	40	37
1.2 Cu + 0.4 Be + 0.2 Fe		7	-	38	37	36
Zr-2*		(13)	-	-	31	28
<u>500°C Exposure</u>						
1.2 Cu + 0.05 Fe		14	291	319	-	490
1.6 Cu + 0.2 Fe		19	121	152	-	407
1.2 Cu + 0.05 Fe*		(13)	-	293	-	294
1.1 Cu + 0.3 Fe*		(13)	-	114	-	244
1.2 Cu + 0.4 Ni + 0.2 Fe		8	78	80	-	165
1.2 Cu + 0.4 Be + 0.2 Fe		7	165	207	-	703
Zr-2*		(13)	-	591	-	1563

\* First Round data. All alloys fabricated by the same schedule: Beta treated, 565°C alpha anneal.



### Fabrication Schedule

The second objective of the second round alloy evaluation was to determine the effect of two alternate fabrication schedules on the performance of a Zr + 2.3 at. % Cr and a Zr + 1.2 at. % Cu alloy. The fabrication schedules and the resulting microstructures were given in detail in the previous quarterly report.<sup>8</sup>

The effect of fabrication schedule on the corrosion resistance and hydrogen content of the two alloys can be assessed from the data in Tables 9 and 10. The most significant conclusion is the excellent performance of the Zr + 2.3 at. % Cr alloy when alpha annealed at 788°C (Schedule C). With this heat treatment, this alloy clearly shows the best performance of any alloy tested in the entire program - both at 300°C and also at 500°C. The higher alpha annealing treatment is also beneficial for the Zr-Cu alloy, but even in this heat treatment the alloy is not as good as the Zr-Cr-Fe alloys are with less favorable heat treatment.

Post-corrosion sheet impact tests at 300°C were performed on all coupons before hydrogen analyses were made. Only the Zr + 2.3 at. % Cr alloy coupon with the least favorable heat treatment (A) exposed 3000 hours at 500°C showed any significant loss of ductility. This coupon contained 961 ppm H<sub>2</sub>. The more ductile (B) and (C) coupons with only 227 to 246 ppm hydrogen after 3000 hours would be expected to go at least 15,000 hours at 500°C before becoming brittle in the 300°C impact test.

### Upper Temperature Limits for Zirconium Alloys in Steam

A study was made of the possible limiting temperatures for the use of zirconium alloys in steam. The results were presented in detail in "The Factors Limiting the Utilization of Zirconium Alloys in Superheated Steam," by H. H. Klepfer and D. L. Douglass, prepared for the American Nuclear Society Meeting, New York, November 20, 1963.<sup>12</sup> The abstract of that paper



TABLE 9. Effect of Fabrication Schedule on Weight Gain  
(Weight Gain, mg/dm<sup>2</sup>)

<u>300°C Exposure</u>							
<u>Alloy Composition</u>	<u>Fabrication Schedule*</u>	<u>175 h</u>	<u>750 h</u>	<u>1125 h</u>	<u>1875 h</u>	<u>2250 h</u>	<u>3000 h</u>
Zr + 2.3 at. % Cr	A	-	13.8	15.0	-	16.9	19.3
	B	-	13.7	14.3	-	16.5	18.8
	C	-	11.3	11.9	-	13.9	15.8
<u>500°C Exposure</u>							
	A	50	123	188	313	-	439
	B	50	99	115	144	-	181
	C	48	95	110	138	-	168
<u>300°C Exposure</u>							
Zr + 1.2 at. % Cu	A**	-	15.7	18.8	-	25.4	26.9
	A	-	17.4	18.3	-	20.1	22.5
	B	-	19.5	20.3	-	23.0	25.5
	C	-	19.5	19.7	-	23.4	25.8
<u>500°C Exposure</u>							
	A**	125	187	214	-	-	360
	A	86	195	213	257	-	323
	B	82	173	187	220	-	294
	C	87	172	188	203	-	238

\* See previous quarterly progress report for complete description. A and B were beta treated. Final anneal: A = 565°C, Band C = 788°C.

\*\* First Round data for alloy 026 which is also Zr + 1.2 at. % Cu.

Sponge zirconium contained 0.05 at. % Fe.



TABLE 10. Effect of Fabrication Schedule on Hydrogen Content

300°C Exposure

Alloy Composition	Fabrication Schedule*	Hydrogen Content (ppm)				
		0	750 h	1125 h	2250 h	3000 h
Zr + 2.3 at. % Cr	A	11	-	16	21	21
	B	9	-	8	10	10
	C	5	-	6	7	7

500°C Exposure

A	11	150	251	-	961
B	9	107	117	-	246
C	5	105	122	-	227

300°C Exposure

Zr + 1.2 at. % Cu	A**	(13)	-	-	63	60
	A	14	-	67	64	65
	B	6	-	38	43	41
	C	5	-	38	41	40
	A**	(13)	-	293	-	494
A	14	291	319	-	490	
B	6	262	262	-	417	
C	5	264	275	-	294	

\* See previous quarterly progress report for complete description: A and B were beta treated. Final anneal: A = 565°C, B and C = 788°C.

\*\* First Round alloy data for alloy 026 which is also Zr + 1.2 at. % Cu.

Sponge zirconium contained 0.05 at. % Fe.



reads as follows:

"New experimental data and literature data are utilized to determine the upper temperature of usefulness of zirconium alloys. Three basic engineering assumptions are used: (1) service life requirements are on the order of four years; (2) tubular fuel cladding for rod-type fuel is considered with a maximum wall thickness of 1.27 cm; and (3) heat fluxes are above 157 watts/cm<sup>2</sup>. The inter-relation of three basic factors, corrosion rate, corrosion embrittlement by hydrogen and oxygen, and strength are considered.

"An upper limit for an acceptable corrosion rate for long-term service of 1 mg/dm<sup>2</sup> is set primarily by the effect of heat transfer on corrosion. For the best alloys anticipated, this requirement (even without considering transient conditions) limits cladding surface temperatures to less than 540°C. Oxygen embrittlement of the alloy substrate by oxide film dissolution is not expected to be a limiting factor. Corrosion hydrogen embrittlement was studied in detail and found to limit acceptable service to cladding surface temperatures of less than 525°C for established experimental alloys. Hydrogen embrittlement may not be a limiting factor if alloys corrosion resistant enough to be acceptable above 600°C could be developed. Zirconium alloys designed for higher strength to overcome their inherent rapid loss of creep strength at temperatures above 540°C are expected to be more susceptible to corrosion hydrogen embrittlement.

"The results of this study indicate that there is good promise for developing zirconium alloys for fuel cladding application at temperatures up to 475°C."



The estimated upper service temperatures for zirconium alloys in steam are summarized:

<u>Limiting Factor</u>	<u>Application</u>			
	<u>Cladding</u>		<u>Structural</u>	
	<u>Developed Alloys, °C</u>	<u>Potential Alloys, °C</u>	<u>Developed Alloys, °C</u>	<u>Potential Alloys, °C</u>
Corrosion	475	540	565	670
Oxygen Embrittlement	>700	>700	*	*
Hydrogen Embrittlement	525	>610	*	*
Creep Strength	540	600	*	*

\* Greater than the corrosion-limited temperature, estimate dependent on design section size.

#### Alloy Selection for Cladding Evaluation

Based on the evaluation data and the derived response curves for corrosion and hydriding rates, an alloy composition has been selected for evaluation as fuel cladding. The pilot fuel assembly will be run in a boiling water core. The alloy was thus selected for optimum performance near 300°C - with the best compromise being made for resistance to over-temperature conditions.

The alloy selected contains Zr + 2.0 ± 0.3 at. % Cr (1.15 ± 0.15 wt. % Cr). Solution of the response curves also gave not only the specification limits on chromium content, but also a maximum limit (1000 ppm) for iron.

In addition to the first round response curves, several other considerations were included in selecting the alloy composition for pilot evaluation as fuel cladding; e.g.,

1. Data on mechanical properties<sup>6</sup> which indicate that the Zr-Cr alloy will have tensile values within 10% of those of Zircaloy-2.
2. Data on post-corrosion mechanical properties which show no significant loss in ductility for Zr-Cr (Fe) alloys in this composition range even when tested at room temperature after exposures at 500°C for 4917 hours: Alloy 019, 26.5% RA with 415 ppm H and Alloy 024, 24.7% RA with 627 ppm H.



3. Second round data (Section III-B) indicate that even lower hydriding rates and less hydrogen embrittlement could be expected for Zr-Cr alloys given a final alpha anneal at 788°C, instead of 565°C as was the case for the first round samples.
4. Our previous data<sup>13</sup> indicate that total hydrogen weight gain for Zr-Cr alloys would be close to a minimum at several test temperatures with chromium content at about 1.0 wt. % Cr.
5. The metallurgical simplicity of a binary Zr-Cr alloy compared to higher order compositions.

The closest alternate candidate for selection was Zr-Cu-Fe which may perform better than Zr-Cr at 500°C. However, the presence of copper apparently leads to higher hydrogen uptake at 300°C than does chromium.

#### ACKNOWLEDGMENTS

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APPENDIX A  
DETERMINATION OF HYDROGEN IN ZIRCONIUM ALLOYS

H. E. Perrine

INTRODUCTION

Zirconium alloy samples for the Zirconium Alloy Design Program were analyzed for hydrogen content by inductively heating them in a high-vacuum system. The hydrogen was transferred into a McLeod gauge for measurement. The apparatus<sup>1</sup> and techniques are described.<sup>2</sup> The accuracy of the analysis is discussed in detail.

SAMPLE SIZE

In general, full-size samples weighing 0.8 gm were used for all pre-autoclave exposure analyses and those in which the hydrogen level was below 100 ppm. When the hydrogen content reached ~ 200 ppm, ~ 0.4-gm samples were used, and ~ 0.2-gm samples were used for 300- to 400-ppm hydrogen level and above.

REAGENTS

Trichloroethylene, reagent grade.

Acetone, reagent grade.

Apiezon W high-vacuum wax.

METHOD OF ANALYSIS

The apparatus used is illustrated in Figures 1 and 2.

The samples are degreased with trichloroethylene and acetone and weighed. No attempt was made to remove the oxide coatings to preserve over-all specimen correlation. Up to 40 samples in duplicate can be loaded in the multiple loading arms. A magnetic pusher is used to transfer the sample from the loading arm into the molybdenum crucible. The sample is inductively heated to



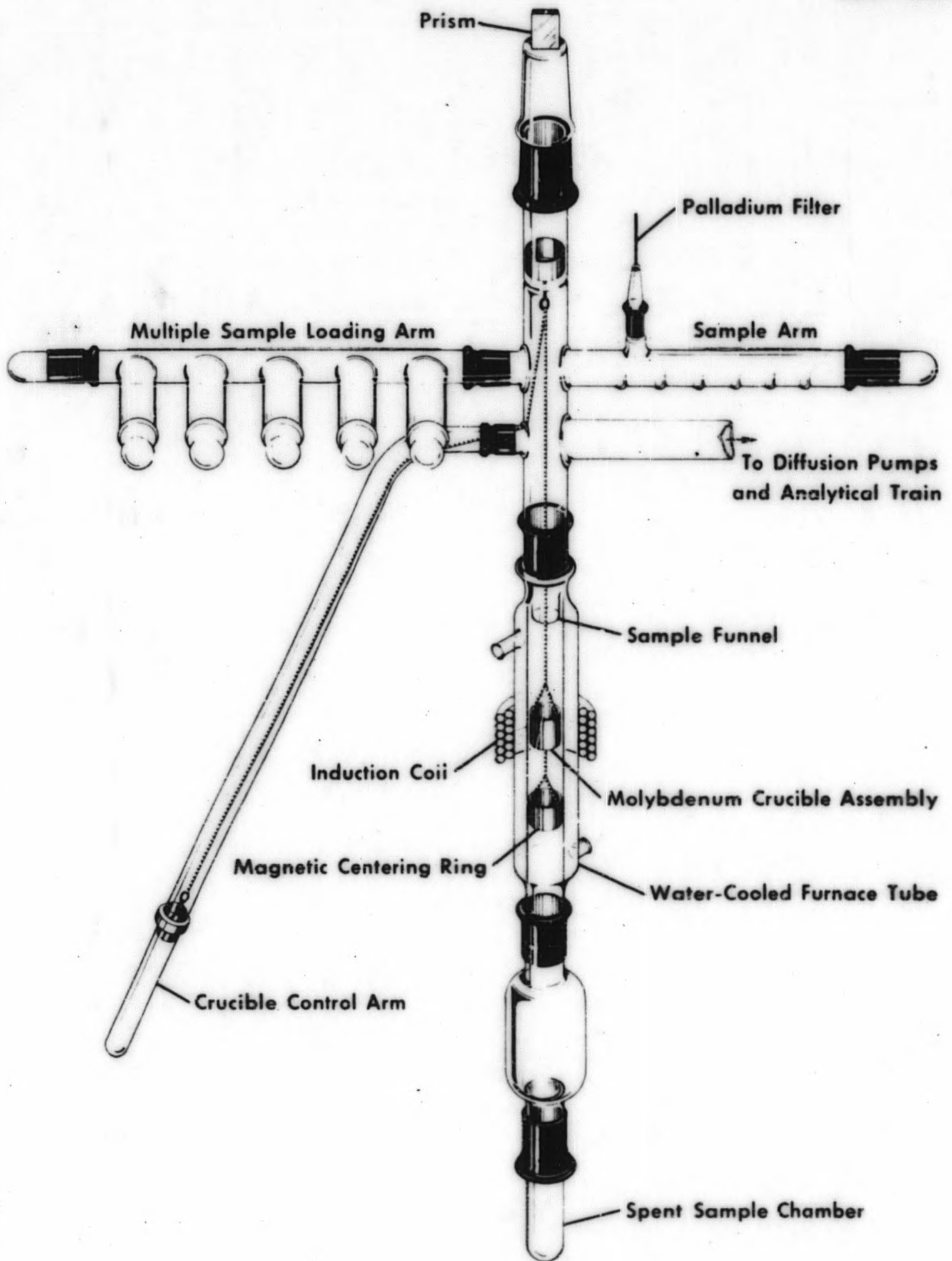


Figure 1. FURNACE AREA OF HYDROGEN ANALYZER



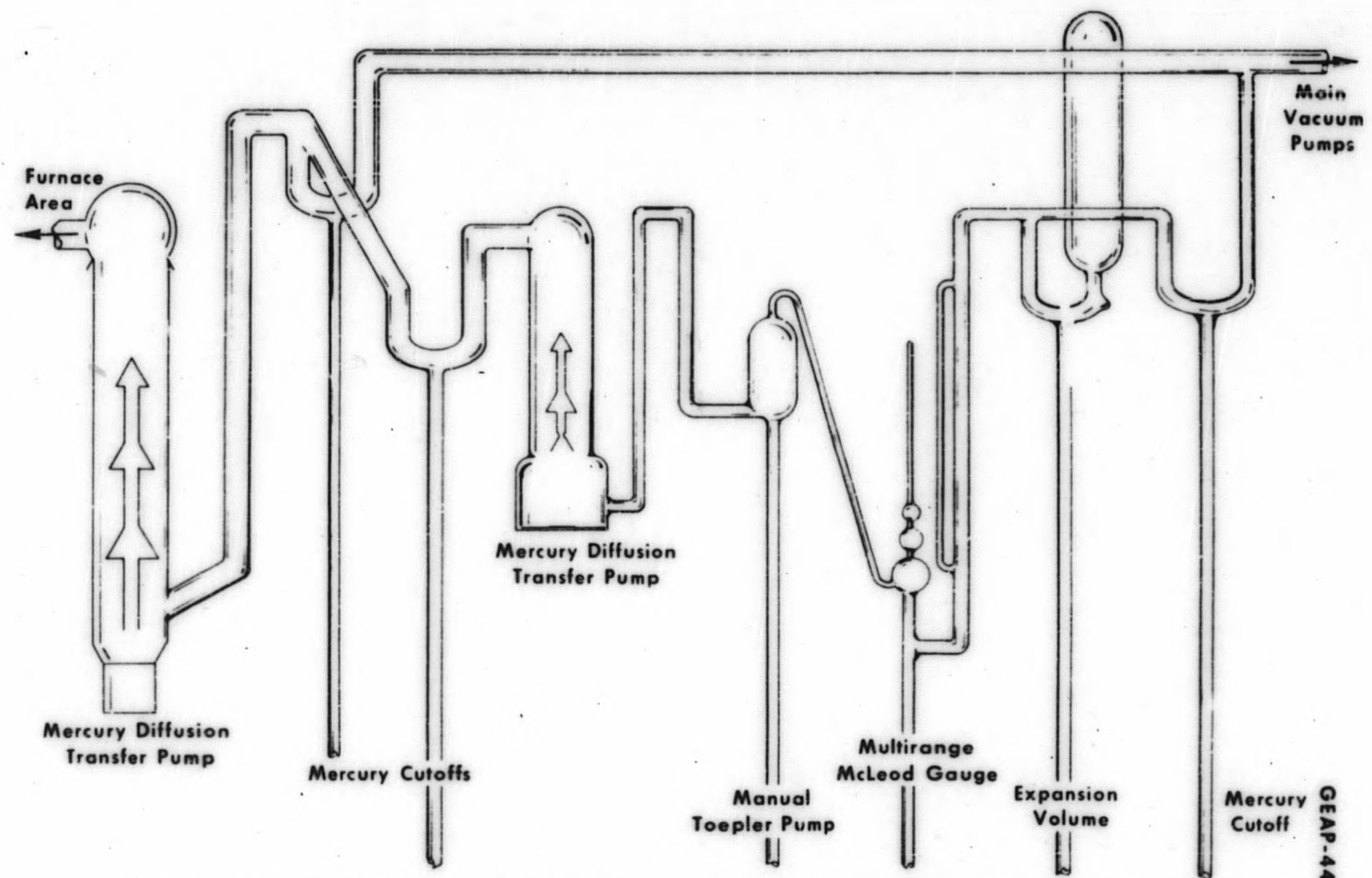


Figure 2. ANALYTICAL TRAIN OF HYDROGEN ANALYZER (Some Mercury Cutoffs not Shown)

VAL 4986  
27

GEAP-4484



1200°C ± 50°C. The hydrogen is removed from the furnace area by mercury diffusion pumps. The first pump is a high-speed (70 l/sec) pump; the second is a lower speed but capable of withstanding a high backing pressure (5 mm). A manual toepler pump is used to pack the hydrogen into the McLeod gauge. The McLeod gauge is of the multirange type with approximate ranges of 0 to 1 mm on the quadratic scale and 0 to 1.5, 0 to 5, and 0 to 17 mm on the three linear scales. If the hydrogen cannot be packed directly into the McLeod gauge, a 500-ml expansion volume is used. The expansion volume is calibrated within 1% by using pure hydrogen from a palladium filter.

After analysis, each sample is dumped from the crucible into the used sample chamber. This ensures that spent samples will not accumulate in the heated zone to affect the instrument blank value. The ASTM requirements for a satisfactory blank are that the system outgassing rate should not exceed 0.3 μ/min.<sup>2</sup> A satisfactory blank is obtained with a clean, high-vacuum system (10<sup>-6</sup> torr) and a crucible outgassing temperature of 1500 to 1700°C. The main vacuum system consists of a 70 l/sec oil diffusion pump and a 2.4 ft<sup>3</sup>/min mechanical backing pump. Mercury cutoffs are used as valves in the high-vacuum system to avoid stopcock leakage. Apiezon W wax is used to seal all standard taper glass joints.

#### HYDROGEN EVOLUTION TIME

Samples with short corrosion exposures evolved all the hydrogen within 20 min or less. However, as the surface oxide layer became heavier with increasing autoclave exposure, it was necessary to increase time or temperature to maintain good precision.

#### BERYLLIUM-CONTAINING SAMPLES

Three of the zirconium alloys under evaluation contained up to 0.8 at. % beryllium. Special precautions were used in the analysis of samples of these beryllium-containing alloys.<sup>3</sup> No spread of beryllium contamination was found beyond the immediate heated area and the spent sample chamber. Most of the contamination was plated on the furnace tube. In general, a wet stainless



steel sponge removed contamination to less than 1  $\mu\text{gm}$  of beryllium. Such cleaning was performed inside the plastic-bag-enclosed furnace assembly and was performed only while a stream of liquid washed down the tube to prevent dust formation. Final cleaning was accomplished with a solution of 1:1  $\text{HNO}_3$  with a few milliliters of HF added. The furnace tube was transferred to a hood for this operation.

#### ACCURACY AND PRECISION

Standards were analyzed concurrently with the zirconium development alloys. The data are presented in Table A-1. National Bureau of Standards samples No. 352 and No. 353 are titanium and not zirconium; however, the method of analysis is the same.

Samples of Zircaloy-2 cladding were also analyzed to give a measure of the precision of the instrument. The data are given in Table A-2.

The over-all coefficients of variation (standard deviation expressed as a percent of the measured value) are 5.6% and 2.4% for the 12- to 30- and 100-ppm ranges, respectively. The 95% confidence limits (95% confidence that the average of a very large number of determinations would be within these limits) are also given in the tables.

#### REFERENCES

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TABLE A-1. Hydrogen Standards Analyzed Concurrently with Development Alloys

Sample	NBS Specified Value (Hydrogen, ppm)	Value Obtained (Hydrogen, ppm)
NPS Standard Sample 352 For Hydrogen Unalloyed Titanium	32 ± 2	28.8
		34.6
		32.0
		30.4
		28.8
		33.1
		34.5
		32.8
		32.3
		32.7
		33.7
		33.9
		32.4
		Average Value = 32.3 ± 1.2 (95% confidence limits)
NBS Standard Sample 353 For Hydrogen Unalloyed Titanium	98 ± 5	Value Obtained (hydrogen, ppm)
		96.4
		95.0
		99.6
		93.8
		100.5
		100.4
		97.5
		95.3
		97.7
		94.0
		98.3
		97.1
98.9		
		Average Value = 97.3 ± 1.4 (95% confidence limits)



TABLE A-2. Zircoloy-2 Cladding Analyzed Concurrently  
with Development Alloys

	<u>Hydrogen, ppm</u>	
Tubing A	17.3	
	17.2	
	16.2	
	16.2	
	16.4	
	17.7	
	18.3	
	17.6	
	16.3	
	19.3	
	18.6	
	19.0	
	18.4	
	Average Value $17.6 \pm 0.6$ (95% confidence limits)	
Tubing R	12.4	
	11.9	
	13.2	
	12.3	
	11.8	
	12.7	
	13.0	
	12.1	
	13.4	
	12.6	
	12.9	
		Average Value $12.6 \pm 0.4$ (95% confidence limits)



APPENDIX B  
COLLECTED METHODS FOR ANALYZING ALLOY COMPOSITION

M. E. Urata

SUMMARY

The detailed chemical methods used to determine the composition of zirconium alloys prepared under Task B of the design program are described. The procedures were taken directly from the literature, and little or no modification of techniques was necessary. Difficulties or precautions necessary are given in the notes following each procedure. Samples of standard materials, NBS and otherwise, were analyzed along with each set of 6 to 8 determinations as a control and as a means of establishing the degree of confidence which could be placed in the composition results.

The detailed methods are described for N<sub>2</sub>, Cr, Fe, Ni, Cu, Sn, and Nb.

DISCUSSION

The compositions of the 31 zirconium alloys prepared under Task B of the Zirconium Alloy Design Program were determined by wet chemical methods. The procedures were adapted from existing literature, and all but one were based on spectrophotometric techniques. A titrimetric method was used for Sn, and it was necessary to dissolve separate, larger alloy samples especially for this analysis. Information pertinent to the analysis of each element is summarized below.

<u>Element</u>	<u>Method</u>	<u>Reagent</u>	<u>Wavelength, m<math>\mu</math></u>	<u>Reference</u>
Fe	Colorimetric	o-Phenanthroline	508	(1)
Ni	Colorimetric	Dimethylglyoxine	540	(1)
Cr	Colorimetric	Diphenylcarbizide	540	(1)
Cu	Colorimetric	Neocuproine	457	(2,3,4)
Nb	Colorimetric	Hydroquinone	410	(5)
N <sub>2</sub>	Kjeldahl	Nessler's	430	(6,7)
Sn	Titrimetric	KIO <sub>3</sub>	---	(8)



A standard Zircaloy sample (NBS 360, Zircaloy-2) was used to establish the precision and accuracy of the Fe, Ni, and Cr analyses. A stainless steel standard (NBS 160A) was used for Cu. For nitrogen, a secondary standard of Zircaloy was used, the value of which had been established by the analytical laboratory at the APED San Jose site. The standard was carried out with each set of 6 to 8 determinations as a control. Consequently, several results were obtained during the time period required for completing the service work. The data tabulated below illustrate the confidence that can be placed in the results of the alloy composition analyses.

<u>Standard</u>	<u>Element</u>	<u>Content</u>	<u>No. of Determinations</u>	<u>Average Value</u>	<u>Deviation, (1 <math>\sigma</math>)</u>
NBS 360	Fe	0.156 wt %	8	0.156	$\pm 0.015$
	Cr	0.114 wt %	8	0.125	$\pm 0.008$
NBS 160A	Cu	0.174 wt %	7	0.172	$\pm 0.001$
Zircaloy	N <sub>2</sub>	45.0 ppm	7	43.0	$\pm 2.5$

The alloy compositions desired were prepared by arc-melting the constituents into an ingot followed by fabrication into sheets. The ingot material was analyzed for nitrogen content before rolling operations started to ensure that a maximum limit of 60 ppm N<sub>2</sub> was not exceeded. Specimens were removed randomly from the edges of the sheet and submitted for determination of alloy content.

Pieces of alloy specimens (~ 1.0 gm) were weighed on an analytical balance and then placed in a 125-ml Erlenmeyer flask. An acid mixture consisting of 1.0 ml concentrated HF, 10 ml 6M HCl, and 10 ml 6M H<sub>2</sub>SO<sub>4</sub> was added, and the contents heated gently on a hot plate. Following solution, which was complete in about 30 min, the contents were filtered through Whatman 4 1H filter paper into a 100-ml volumetric flask. The Erlenmeyer flask and filter paper were thoroughly rinsed with distilled water which was added to the volumetric flask with enough additional distilled water to bring the total up to volume.

This solution provided the aliquots which were used for the spectrophotometric analyses described in detail in the pages that follow. When Sn analyses were required, a separate sample of alloy material was treated as indicated in the Sn procedure.



## NITROGEN

PRINCIPLE

Small amounts of nitrogen in zirconium or in zirconium-base alloys are determined by using the Kjeldahl method. Dissolution of the sample in hydrochloric and hydrofluoric acids converts nitrides and solid solutions of nitrogen into an ammonium salt. An excess of sodium hydroxide is added to the mixture, and ammonia is liberated by steam-distillation, collected, and analyzed colorimetrically with Nessler's reagent. The method covers the range of 10 to 1000 ppm of nitrogen. The range can be varied by varying the sample size, the wavelength, and the path-length of the solution used for photometric measurement.

REAGENTS AND APPARATUS

HF, concentrated.

HCl, 6M.

NaOH, 15M. Dissolve 600 gm of NaOH in 1000 ml of distilled water.

Nessler Reagent. Dissolve 50 gm  $\text{HgI}_2$  and 35 gm KI in a small quantity of ammonia-free water. Add this mixture slowly, stirring constantly, to 250 ml of 8M NaOH. Dilute to 1 liter with ammonia-free water.

The reagent does not deteriorate and can be stored indefinitely.

Standard Nitrogen solution, 10.04  $\mu\text{gm N/ml}$ . Dissolve 1.909 gm of  $\text{NH}_4\text{Cl}$  in distilled water and dilute to 500 ml. Pipet 10.00 ml of this stock solution and dilute to 1 liter with distilled water.

Ammonia-free water. Pass distilled water through a mixed-bed resin demineralizer.

Distilling Apparatus - Micro-Kjeldahl. Western Scientific Apparatus, W2870.

Beckman DU Spectrophotometer, or equivalent.



PROCEDUREA. Calibration Curve

1. Pipette 0 (blank), 2, 4, 6, 8, 10, and 12 ml of the standard nitrogen solution (10.04  $\mu\text{g/ml}$ ) into a 50-ml volumetric flask containing 25 to 30 ml of ammonia-free water.
2. Add 1 ml of Nessler's reagent, dilute to the mark with distilled water, and shake well.
3. Determine the optical density of the standard solutions at 430  $m\mu$  in 1.00 cm cells.
4. Subtract the blank reading and plot the values against micrograms of nitrogen.

B. Samples

1. Place a weighed sample ( $\sim 1.0$  gm) into the 50-ml distillation flask used with the micro-Kjeldahl apparatus.
2. Add 15 ml 6M HCl and 1 ml concentrated HF. Heat until dissolution is complete and allow the solution to cool to room temperature. (Note 1).
3. Fill the steam-generating flask with ammonia-free water ( $\sim 400$  ml). Heat and pass steam through the distillation flask into the condenser. Collect and test the distillate for ammonia with Nessler's reagent until the test is negative.
4. Add 25 ml of 15M NaOH to the dissolver solution cautiously to form two layers in the flask. Immediately attach the distillation flask to the rest of the apparatus.
5. Steam-distill for about 7 min or until 35 to 50 ml of distillate is collected.
6. Remove the distillation flask and the 50-ml volumetric flask from the apparatus.
7. Add 1.0 ml of Nessler's reagent to the volumetric flask and dilute to the mark with ammonia-free water. Shake well.



8. Measure the optical density on a spectrophotometer at 430  $m\mu$ , by using 1.0-cm cells. Carry a reagent blank throughout the procedure and correct the optical density of the sample for this amount.
9. Refer to the calibration curve prepared above and determine the amount of N from the calibration curve. (Note 2)

#### CALCULATIONS

$$\frac{\mu\text{gm N}}{\text{gm sample}} = \text{ppm N}$$

#### NOTES

1. The ingot solution is light green and contains a small amount of insoluble  $\text{SiO}_2$ .
2. Standards and samples (including blanks) should be prepared and read on the instrument at the same time.



## CHROMIUM

PRINCIPLE

This method is based on the colorimetric determination of  $\text{Cr}^{+6}$ , which forms a soluble, purple-red complex in an acid medium with diphenylcarbozide. The reaction is very sensitive, and permits analysis of Cr content as low as  $0.05 \mu\text{g}/\text{ml}$ . Large amounts of Mo interfere. The optical density is measured as  $540 \text{ m}\mu$ , and the amount of Cr is determined from a calibration curve prepared with a standardized Cr solution.

REAGENTS AND APPARATUS

$\text{AgNO}_3$ , 0.015M. Dissolve 0.625 gm  $\text{AgNO}_3$  in distilled water and dilute to 250 ml. Prepare a fresh solution daily.

$\text{HNO}_3$ , concentrated

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution, 10% by weight, in distilled water.

Diphenylcarbozide reagent. Dissolve 0.32 gm of diphenylcarbozide and 4.0 gm of phthalic anhydride in 100 ml of ethanol. Place in a dark bottle. A fresh solution must be prepared daily.

Standard Cr solution,  $6.0 \mu\text{g}/\text{ml}$ . Dissolve 0.1695 gm of  $\text{K}_2\text{Cr}_2\text{O}_7$  in distilled water and dilute to 1 liter. Pipet accurately 10.00 ml of this solution into a 100-ml volumetric flask and dilute to volume with distilled water.

Beckman DU or DB spectrophotometer, or equivalent.

PROCEDURE

1. Pipet an aliquot of dissolved alloy solution that contains from 2 to  $30 \mu\text{g}$  of Cr, (see p. 33), and place in a 100-ml beaker. Add 2 ml of concentrated  $\text{HNO}_3$  and boil the contents to dryness. Cool, add 5 ml of concentrated  $\text{HNO}_3$ , and take to dryness a second time.
2. Add 10 ml of distilled water and 5 ml of  $\text{AgNO}_3$  solution. Heat to a rolling boil. Add 2 to 3 ml of 10%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and boil for 10 min longer.



3. Transfer the solution to a 50-ml volumetric flask and rinse the beaker with distilled water. Cool in an ice bath to below room temperature ( $\sim 150^{\circ}\text{C}$ ).
4. Add 2.00 ml of diphenylcarbozide reagent, dilute to volume with distilled water, and shake well.
5. Transfer the contents to 1-, 4-, or 10-cm cells (depending on the sensitivity desired) and measure the optical density at 540 m $\mu$  within 5 min after completing Step 4. (Note 1)
6. Carry a reagent blank through the procedure, and correct the optical density of the sample for this value.
7. Refer to a calibration curve prepared by taking suitable aliquots of the standardized Cr solution and following Steps 1 through 6. Record the micrograms of Cr corresponding to the optical density of the sample, after the blank value has been subtracted.

#### CALCULATIONS

$$\frac{\mu\text{gm Cr} \times V_1}{V_2 \times \text{alloy wt (gm)} \times 10^6} \times 100 = \text{wt \% Cr}$$

where

$V_1$  = Volume of dissolver solution, ml (see p. 33) and

$V_2$  = Volume of aliquot, ml, removed for Cr analysis.

#### NOTES

1. The color of the chromium-diphenylcarbozide complex develops almost immediately upon addition of the reagent, but starts to fade within a short period of time.



## IRON

PRINCIPLE

Iron is determined by measuring the intensity of the orange-red complex formed between  $\text{Fe}^{++}$  and o-phenanthroline. The color intensity is not very pH dependent, and the  $\left[ (\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Fe} \right]^{++}$  complex is very stable. Optical density measurements are made at 508 m $\mu$  and the Fe content is calculated from a calibration curve plotted from data obtained by using a standardized Fe solution run in the same manner.

REAGENTS AND APPARATUS

$\text{NH}_2\text{OH}\cdot\text{HCl}$ , 10%. Dissolve 10 gm of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 90 ml of distilled water.

O-phenanthroline, 0.1%. Dissolve 0.5 o-phenanthroline in 5 drops concentrated HCl and 1 ml of distilled water. Add 100 ml of distilled water, 200 gm of sodium acetate, and 200 ml of glacial acetic acid. Warm, stir until dissolved, and dilute to 500 ml with distilled water.

Standard Iron solution, 10.00  $\mu\text{gm Fe/ml}$ . Dissolve 0.1000 gm of pure iron wire in a minimum of 6M HCl and dilute to 1 liter with distilled water.

Beckman DU Spectrophotometer, or equivalent.

PROCEDURE

1. Pipet accurately in aliquot containing from 1 to 20  $\mu\text{gm Fe}$  from the stock solution of dissolved alloy (see p. 33), and transfer it to a 25-ml volumetric flask containing about 15 ml of distilled water.
2. Add 2.0 ml of 10%  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution. Mix well.
3. Add 1.0 ml of o-phenanthroline and swirl the contents until completely mixed. Test the pH of the solution with pH paper, and adjust with 0.01M HCl or 0.01M  $\text{NH}_4\text{OH}$  if necessary to attain the value of 3-5.



4. Let the solution stand for 30 min to ensure complete reduction of iron to  $\text{Fe}^{++}$ , then dilute to volume with distilled water. Mix thoroughly.
5. Transfer the solution to a 4-cm cell and measure the optical density at 508  $\text{m}\mu$  on a spectrophotometer. Carry a reagent blank through the procedure also.
6. Subtract the blank value from the optical density of the sample. Refer to a plot of outside diameter versus micrograms Fe, prepared by using the standardized Fe solution, to determine the Fe content of the sample.

#### CALCULATIONS

$$\frac{\mu\text{gm Fe} \times V_1}{V_2 \times \text{alloy wt (gm)} \times 10^6} \times 100 = \text{wt \% Fe}$$

where

$V_1$  = Volume of dissolver solution, ml (see p. 33) and

$V_2$  = Volume of aliquot, ml, taken for Fe analysis (Step 1).



## NICKEL

PRINCIPLE

The determination of Ni is accomplished by measuring the absorption of the wine-red complex formed with dimethylglyoxime in an ammonium medium. Bromine is used as an acidifier. To calculate the Ni content, the optical density read at 540 m $\mu$  is referred to a calibration curve plotted from the measurements of standardized Ni solutions of varying contents.

REAGENTS AND APPARATUS

NH<sub>4</sub>OH, concentrated.

Citric acid, 10%.

H<sub>3</sub>BO<sub>3</sub>, 0.85M. Dissolve 26.3 gm H<sub>3</sub>BO<sub>3</sub> in hot, distilled water, cool, and dilute to 500 ml.

Bromine water saturated. Keep in a glass-stoppered bottle. Shake before using.

Dimethylglyoxime, 1.0%. Dissolve 1.0 gm dimethylglyoxime in ethanol and dilute to 100 ml.

Standard Ni solution, 15.0  $\mu$ gm Ni/ml. Dissolve 0.6075 gm NiCl<sub>2</sub>·6H<sub>2</sub>O in distilled water and dilute to 1 liter. Pipet accurately 10.00 ml of the solution and transfer to a 100-ml volumetric flask with sufficient distilled water to make to volume.

PROCEDURE

1. Pipet accurately an aliquot containing from 1 to 50  $\mu$ gm of Ni from the stock solution of dissolved alloy (see p. 33) and transfer it to a 50-ml volumetric flask. Add 5.0 ml of 10% citric acid and swirl until the solution is homogeneous.
2. Add 2.0 ml of Br<sub>2</sub> water and 2.5 ml of 0.85M H<sub>3</sub>BO<sub>3</sub>. Mix, and allow the solution to stand for 5 min.



3. Add concentrated  $\text{NH}_4\text{OH}$  dropwise, with swirling, until the yellow color just disappears; then add 3.0 ml more. Cool the contents in an ice bath until the temperature is below  $20^\circ\text{C}$ .
4. Remove the flask from the ice bath, and add 0.50 ml of 1% dimethylglyoxime reagent and mix well. Allow the solution to stand for 15 min, then dilute to volume with distilled water.
5. Transfer the solution to a 4-cm cell and measure the optical density at 540  $\text{m}\mu$  on a spectrophotometer. Carry a reagent blank through the procedure also.
6. Subtract the blank value from the optical density of the sample. Refer to a plot of outside diameter versus micrograms Ni, prepared by using the standardized Ni solution, to determine the Ni content of the sample.

#### CALCULATIONS

$$\frac{\mu\text{gm Ni} \times V_1}{V_2 \times \text{alloy wt (gm)} \times 10^6} \times 100 = \text{wt \% Ni}$$

where

$V_1$  = Volume of dissolver solution, ml (see p. 33) and

$V_2$  = Volume of aliquot, ml, taken for Ni analysis (Step 1).



COPPERPRINCIPLE

Copper (I) forms a yellow complex with neocuproine (2, 9-dimethyl-1, 10-phenanthroline), which is a specific reagent for this element. The Cu in the alloy mixture is reduced to the univalent state with hydroxylamine, and the complex is extracted into chloroform. The optical density of the organic phase is measured at 457 m $\mu$  on a spectrophotometer. The Cu content is determined from a calibration curve plotted from data obtained by using the standardized Cu solution run in the same manner.

REAGENTS AND APPARATUS

NH<sub>4</sub>OH, concentrated.

NH<sub>2</sub>OH.HCl, 10%. Dissolve 10 gm of NH<sub>2</sub>OH.HCl in 90 ml of distilled water.

Sodium citrate, 30%. Dissolve 30 gm Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>.2H<sub>2</sub>O in 70 ml of distilled water.

Neocuproine, 0.1%. Dissolve 0.10 gm of neocuproine in a minimum of ethanol and dilute to 100 ml.

CHCl<sub>3</sub>, reagent grade.

Ethanol, absolute, reagent grade.

Standard Cu solution, 10  $\mu$ gm Cu/ml. Dissolve 0.1000 gm of pure Cu metal in a minimum of 1:1 H<sub>2</sub>SO<sub>4</sub> and dilute to 1 liter with distilled water. Pipet 10.00 ml of this solution and transfer it to a 100-ml volumetric flask and enough distilled water to make to volume.

Beckman DU Spectrophotometer, or equivalent.

PROCEDURE

1. Pipet accurately an aliquot containing not more than 20  $\mu$ gm of Cu from the stock solution of dissolved alloy (see p. 33), and transfer it to a 125-ml separatory funnel. Add 5.0 ml of 10% NH<sub>2</sub>OH.HCl and 10.0 ml of 30% sodium citrate. (Note 1)



2. Add concentrated  $\text{NH}_4\text{OH}$  until the pH lies between 4 and 6 (pH paper).
3. Add exactly 10.00 ml of 0.1% neocuproine and 10.0 ml of  $\text{CHCl}_3$ . Shake for 30 sec, then allow time for the phases to separate cleanly.  
(Notes 2, 3)
4. Draw off the  $\text{CHCl}_3$  layer into a 25-ml volumetric flask containing 3 to 4 ml of absolute ethanol.
5. Extract again with 5.0 ml of fresh  $\text{CHCl}_3$  and draw off the bottom layer into the volumetric flask as in Steps 3 and 4. Dilute to volume with absolute ethanol and mix thoroughly.
6. Transfer the solution to a 1-cm cell and measure the optical density at 457  $\mu$  on a spectrophotometer. Carry a reagent blank through the procedure also.
7. Subtract the blank value from the optical density of the sample. Refer to a plot of outside diameter versus micrograms Cu prepared by using the standardized Cu solution to determine the Cu content of the sample.

#### CALCULATIONS

$$\frac{\mu\text{gm Cu} \times V_1}{V_2 \times \text{alloy wt (gm)} \times 10^6} \times 100 = \text{wt \% Cu}$$

where

$V_1$  = Volume of dissolver solution, ml (see p. 33) and

$V_2$  = Volume of aliquot, ml, taken for Cu analysis (Step 1).

#### NOTES

1. Citrates help complex other metallic ions present.
2.  $\text{CHCl}_3$  is recommended over isoamyl alcohol as an extractant because some lots can contain oxidizing impurities which can lead to erroneous results.
3. The volume of the aqueous phase may be as high as 100 ml without loss of Cu in the extraction.
4. The procedure will tolerate up to 10%  $\text{HClO}_4$  and up to 2%  $\text{F}^-$ .



## TIN

PRINCIPLE

Tin is determined in zirconium alloys by the iodometric method. This consists of quantitative reduction of Sn to the bivalent state by elemental lead under an inert gas environment (such as CO<sub>2</sub>) to exclude re-oxidation by air. The Sn<sup>++</sup> is then titrated with standardized KIO<sub>3</sub> to a thyodene end-point (blue).

REAGENTS AND APPARATUS

HCl, 6M.

HF, concentrated.

KIO<sub>3</sub>, 0.05M. Dissolve 1.788 gm of KIO<sub>3</sub> in 50 ml of distilled water containing 0.25 gm of NaOH, and 7.5 gm of KI. Dilute to 1 liter with distilled water, mix, and allow to stand for several days. Standardize this solution against tin metal, 30 mesh, that has been weighed accurately, according to the procedure described below.

CO<sub>2</sub> gas, tank cylinder.

Thyodene indicator.

PROCEDURE

1. Accurately weigh 1.00 gm of alloy sample and transfer to 250-ml Erlenmeyer flask. Add 50 ml 6M HCl, and 2 ml concentrated HF. After solution is complete, add about 50 ml of distilled water. (Note 1)
2. Place the flask on a hot plate and heat to near boiling. Add 1.0 gm of Pb metal, and quickly place a specially prepared 3-hole stopper in the mouth of the flask. (Note 2)
3. Adjust the CO<sub>2</sub> pressure to give a moderately rapid flushing action, and allow the solution to boil for 30 min to ensure complete reduction to Sn<sup>++</sup>.
4. Remove the flask from the hot plate, allow it to cool in an ice bath for 15 to 20 min.



5. Place the flask on a magnetic stirrer, add a few crystals of thyodene, replace the stopper, and titrate to the blue end point with the standardized  $\text{KIO}_3$  solution. Maintain the  $\text{CO}_2$  atmosphere in the void volume of the flask. Record the milliliter titrant required.
6. Carry a blank determination through Steps 1 through 5, using the same amounts of all reagents required for an alloy sample.

### CALCULATIONS

$$\frac{(A-B) \times C}{D} \times 100 = \text{wt \% Sn}$$

where

- A = ml  $\text{KIO}_3$  required for the alloy sample,
- B = ml  $\text{KIO}_3$  required for the blank,
- C = Sn equivalent of the standardized  $\text{KIO}_3$  solution,  
gm Sn/ml  $\text{KIO}_3$ , and
- D = Weight of alloy sample, gm.

### NOTES

1. If the alloy has a nominal composition of  $< 0.2$  wt % Sn, use a 2.00-gm sample.
2. The 3 holes permit introduction of a:
  - a. Glass elbow (to which tygon tubing from the pressure regulator valve of the  $\text{CO}_2$  tank is attached),
  - b. 12 mm o.d., Pyrex glass tube that has been constricted with a file point to support about a 1-inch column of glass beads (as a refluxing surface), and
  - c. Buret tip.

All apparatus is to be so arranged and so handled that the chance for exposure of the aqueous surface to air is eliminated, otherwise the method will possess a negative bias.



## NIOBIUM

PRINCIPLE

Niobium in amounts between 25 and 1000  $\mu\text{gm}$  can be extracted into hexone from an  $\text{H}_2\text{SO}_4$  - HF acid medium. After destruction of the organic phase, the Nb is picked up in concentrated  $\text{H}_2\text{SO}_4$  and hydroquinone is added to produce a yellow-colored niobium complex whose optical density is measured at 410  $\text{m}\mu$  with a spectrophotometer. The Nb content is determined by referring to a calibration curve prepared with a standardized Nb solution carried through the same procedure. Only Ta and large amounts of Mo interfere seriously with the method.

REAGENTS AND APPARATUS

$\text{H}_2\text{SO}_4$ , concentrated.

HF, concentrated.

HF, 4M.

NaOH, 5M.

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ , crystals.

Hexone (4-methyl,2-pentanone).

Hydroquinone solution. Dissolve 5.5 gm of hydroquinone in 100 ml of concentrated  $\text{H}_2\text{SO}_4$ . Prepare a fresh solution daily.

Standard Nb solution, 10.0  $\mu\text{g}$  Nb/ml. Place 0.1000 gm of pure Nb metal in a platinum dish. Add 3 to 5 ml of 7M  $\text{HNO}_3$  and 10 ml of concentrated  $\text{H}_2\text{SO}_4$ . Add concentrated HF dropwise to maintain a slow reaction rate. When solution is complete, evaporate the contents to dense fumes of  $\text{SO}_3$ , transfer the cooled solution to a 1-liter volumetric flask, and dilute to volume with distilled water. Pipet accurately 10.00 ml of this solution and transfer to a 100-ml volumetric flask and make up to volume with distilled water.



PROCEDURE

1. Pipet an aliquot of the dissolved alloy solution that contains from 20 to 180  $\mu\text{gm}$  of Nb, (see p.33), and place it in a 100-ml Pt dish. Add 3.5 ml concentrated  $\text{H}_2\text{SO}_4$  cautiously and evaporate to  $\text{SO}_3$  fumes.
2. Transfer the cooled sample to a 40-ml hevi-wall centrifuge cone using 2.0 ml of distilled water as transferring agent. Swirl to mix and cool the contents further in an ice bath. (Note 1)
3. Rinse the Pt dish with 4.0 ml of 4M HF, and then with 0.5 ml of distilled water, add the rinses to the centrifuge cone.
4. Add 10.0 ml of hexone to the cold solution and stir for 5 min with an efficient pump-mix stirrer. Allow the phases to separate. (Note 2)
5. Pipet accurately 8.00 ml of the hexone layer and transfer it to a platinum dish containing 4 to 5 drops of 5M NaOH. Evaporate the contents to dryness slowly, with frequent swirling to prevent charring. Cool the dish, then add 10 drops of distilled water, 5 drops of concentrated HF, and then 3.5 ml of concentrated  $\text{H}_2\text{SO}_4$  slowly, and with caution.
6. Evaporate the contents to dense fumes of  $\text{SO}_3$ . Perform a second extraction by repeating Steps 2 through 5.
7. Add 5 to 10 mg of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  crystals to the acid solution, and warm the dish on a hot plate until gas evolution ceases and the acid solution is colorless. Continue heating for 3 to 5 min (a heat lamp provides extra help) until very strong fumes of  $\text{SO}_3$  are evolved.
8. Cool, and transfer the contents to a 25-ml volumetric flask, use small portions of concentrated  $\text{H}_2\text{SO}_4$  to rinse the dish.
9. Add 3.00 ml of hydroquinone reagent and dilute to volume with concentrated  $\text{H}_2\text{SO}_4$ . Mix thoroughly. (Note 3)
10. Measure the optical density on a spectrophotometer at 410  $\text{m}\mu$  within 15 min after adding the hydroquinone. Use a reagent blank carried through with the sample as the reference solution.
11. Determine the Nb content by referring to a calibration curve prepared with the standard Nb solution carried through Steps 1 through 10. The curve varies a little with each set of analyses; a new curve should be prepared each time.



CALCULATIONS

$$\frac{\mu\text{gm Nb} \times V_1}{0.8 \times V_2 \times \text{alloy wt (gm)} \times 10^6} \times 100 = \text{wt \% Nb}$$

where

$V_1$  = Volume of dissolver solution, ml (see p. 33) and

$V_2$  = Volume of aliquot, ml, removed for Nb analysis.

NOTES

1. Accurately measure the water used because an excess amount decreases the extraction coefficient of Nb.
2. Such a stirrer was prepared by blowing a bulged section about  $\frac{1}{2}$  inch to  $\frac{1}{2}$  inch long in a piece of  $\frac{1}{4}$  inch o.d. Pyrex tubing. Small holes were made in this section with a sharp pointed instrument. The end about  $\frac{1}{2}$  inch above the bulb was joined to a piece of  $\frac{1}{4}$  inch glass rod, while about 1- $\frac{1}{2}$  inches of the other end were cut and fire polished. The dimensions were such that when inserted in the hexone-aqueous medium, the bulb was located in the organic phase, while the tube-end extended near to the bottom into the aqueous phase. An efficient pump-mix action was possible when the rod-end was inserted into the chuck of a shirring motor.



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