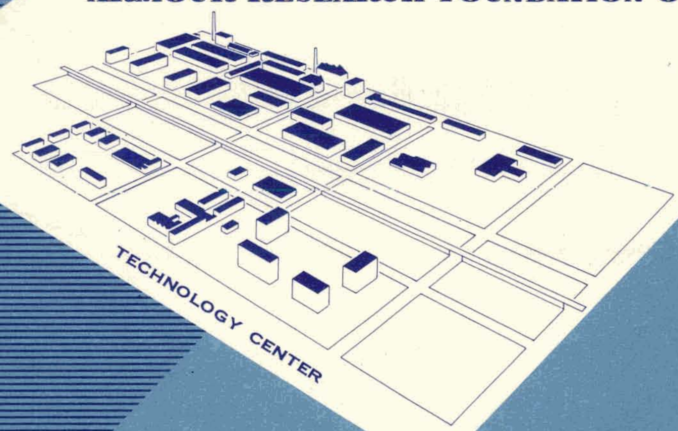
JOINT U.S. - EURATOM RESEARCH AND DEVELOPMENT PROGRAM

MASTER

ARF 2198-28
(EURAEC-347)

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY



IMPROVED ZIRCONIUM ALLOYS

U.S. /EURATOM Program
Contract No. AT(11-1)-578
Project Agreement No. 1

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ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
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IMPROVED ZIRCONIUM ALLOYS

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ARF 2198-28
(Quarterly Report)
January 1, 1962 - March 31, 1962
(EURAEC - 341)

Contract No. AT(11-1)-578
Project Agreement No. 1

U.S./EURATOM Program
Joint Research and Development Board
51-53 rue Belliard
Brussels, Belgium

April 6, 1962

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IMPROVED ZIRCONIUM ALLOYS

I. INTRODUCTION

The United States and the European Atomic Energy Community (EURATOM), on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U.S.-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 U.S.-Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

II. SUMMARY OF PROGRESS TO DATE

The approach to development of successful zirconium alloys has been screening of corrosion properties in superheated water and steam followed by preparation of further compositions based on these corrosion results. Thus, during the first year of work, the major program effort involved determination of the corrosion properties of approximately 100 binary alloys in 680°F water and 750°F steam; selected materials were evaluated in 900°F steam (see ARF 2198-11 and ARF 2198-18).

At the beginning of the current year, data on the corrosion screening studies were available which indicated fifteen binary compositions for further investigation as ternary bases or minor ternary additions for improved corrosion resistance. Thus, approximately 75 ternary compositions were prepared from these alloys (see ARF 2198-18), and the major effort this year has been devoted to ascertaining and evaluating corrosion behavior of these materials.

Corrosion data in 680°F water for these ternary alloys are presently available for an exposure time of 3000 hours. This test duration has allowed for reliable evaluation of materials with respect to corrosion resistance and has indicated that several compositions initially satisfy one of the program objectives. Moreover, these data indicate that further improvement of properties might be realized by minor modifications of alloying concentrations. A further group of about 40 alloys is, therefore, being prepared for optimization of corrosion properties in 680°F water and strength at this temperature. In addition, data on ternary compositions in 750°F steam are available for a 1200-hour exposure which indicate some initially promising alloys. Selected ternary materials have been exposed to 900°F steam for a relatively short time; no definite property evaluations can be made at this time.

III. PRINCIPAL INVESTIGATORS

D. Weinstein	-	Project Engineer
F. C. Holtz	-	Group Leader

IV. STATEMENT OF PROBLEM

The program objectives are the development of zirconium-base alloys having corrosion resistance and/or strength (with equivalent corrosion resistance) markedly superior to Zircaloy-2 in 680°F water and/or 750° to 900°F steam. The pickup of hydrogen during corrosion is also an important aspect of this program; however, this factor is employed for evaluation of experimental alloys rather than as a criterion for screening and development of material.

V. DESCRIPTION OF WORK--RESULTS

The corrosion behavior of ternary experimental alloys in 680°F water for a duration of 3000 hours is presented in Table I. A detailed analysis of these data was presented in the last Quarterly Report (ARF 2198-24) and a recently issued Summary Progress Report (ARF 2198-26) which gives tensile properties of these alloys as well. The corrosion behavior of promising alloys is essentially unchanged from previous results at 2000 hours; that is, these alloys continue to exhibit better corrosion resistance to 680°F water than Zircaloy-2. Graphically, these results are represented in Figure 1 and Figure 2. Zircaloy-2, plotted here for comparison purposes, exhibits breakaway corrosion after approximately 100 days (30 mg/dm^2) which agrees with Bettis data on identical material. In Figure 1, the three experimental alloys have not, apparently, reached a transition, and the corrosion rate after 3000 hours is considerably lower than Zircaloy-2. In Figure 2, the Zr-1Cr-0.25Te and Zr-1Sb-0.25Te alloys show similar behavior; however, the Zr-1Sb-0.5Nb alloy exhibits a rather early transition followed by a lower post-transition corrosion rate than Zircaloy-2. Thus, after 3000 hours, the latter composition is also better than Zircaloy-2. Further data are being obtained on these materials to establish corrosion properties more accurately.

As previously related, the choice of ternary compositions for study in 750°F steam was based on corrosion results of binary alloys exposed to this medium. Table II lists the ternary alloys presently being studied in 750°F steam and summarizes the corrosion behavior for a 1200-hour exposure time. Although a longer time of test is desired before expounding on the merits of various alloys, at least certain trends in corrosion behavior of these materials are now apparent. In particular, the alloys Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe thus far exhibit good corrosion properties and ought to have excellent elevated temperature strength. Alloys which also show good corrosion resistance are Zr-0.5Nb-0.25(Cr, Te), Zr-1Fe-0.25(Cr, Te) and perhaps Zr-1Sb-0.25Te; in these materials, with the possible exception of the latter one, a further increase in strength would probably be necessary for consideration as useful compositions. At present, potentially useful alloys have been returned to the autoclave so that more meaningful evaluation of corrosion behavior can be made.

During this report period, initial corrosion data were obtained on alloys received from General Nuclear Engineering Corporation. These compositions were originally prepared for study under a program on CO_2 corrosion resistance of zirconium;[1] in exchange, ARF forwarded a number of binary alloys from the present program to GNEC. The corrosion properties of GNEC alloys in 680°F water for a rather short exposure time are

(1) W. Maxwell, GNEC, private communication.

summarized in Table III. In general, the corrosion resistance of these alloys is poor with the exception of alloys containing chromium, beryllium, tellurium, and perhaps palladium. Since the test duration is relatively short, no definite conclusions can be advanced and no evidence is yet available indicating incorporation of certain GNEC alloys into the present program. Further exposure to 680°F water is presently being carried out; when autoclave space becomes available, these materials will be evaluated in 750°F steam.

VI. FUTURE WORK

Work on optimization of corrosion and strength properties of promising ternary alloys for 680°F water by variations of alloy content will be initiated during the next quarter. At present, all compositions (see ARF 2198-26) have been arc-melted and are being fabricated to corrosion coupons for autoclave exposure. For 750°F steam, data for an exposure time of approximately 3000 hours will be obtained, and alloys based on promising materials and designed for optimization of corrosion and strength properties will be prepared. Additional data on compositions for 900°F steam will be obtained, and any indications of promising materials will be investigated by preparation of selected alloys.

The pickup of corrosion hydrogen is an important consideration in utilization of an alloy as a cladding material. Unfortunately, to obtain this information requires destruction of the corrosion specimen. Moreover, various investigations have reported inconsistent data on behavior characteristics in the rate at which hydrogen is absorbed; in some cases, weight gain due to hydrogen closely follows the corrosion curve due to oxygen absorption and subsequent oxide formation whereas, in others, a decrease in hydrogen pickup has been observed as the corrosion process proceeds. It would seem, therefore, that more meaningful data would be obtained on specimens exposed for a period of time sufficient to accurately define the corrosion properties due to oxygen. For the promising alloys in 680°F water, hydrogen pickup characteristics will be determined when the corrosion behavior is well defined; reliable data will be obtained at 4000 or 5000 hours' exposure, at which time the amount of hydrogen absorbed will be determined. This work will be carried out during the next quarter.

VII. CONCLUSIONS

This program is concerned with development of zirconium-base alloys having corrosion resistance and strength superior to Zircaloy-2 and/or development of materials of equivalent corrosion resistance but exhibiting enhanced strength. The current investigations on ternary alloys resulted from an extensive binary alloy corrosion screening study carried out during the first year; after approximately 2000 hours' exposure to 680°F water, a number of compositions were selected for further alloy modification. After 3000 hours' exposure, these alloys continue to show corrosion resistance superior to Zircaloy-2; hopefully, a number of these compositions will initially satisfy the program objectives. Alloys which are considered promising and offer the highest chance of success are based on the binary compositions Zr-1Cr, Zr-1Sb, Zr-0.5Nb, and Zr-0.5Sn with small additions of Te, Ge, Cr, or Fe. Alloys containing relatively high percentages of solute elements have not exhibited satisfactory corrosion properties; very little further effort will be devoted to these compositions as applied to materials for resistance to superheated water.

Corrosion data on experimental alloys in 750°F steam environment indicate a few highly promising and initially acceptable materials. The salient alloys of this group are Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe; thus far the corrosion resistance is better than Zircaloy-2 and the higher alloy content indicates enhanced elevated-temperature strength.

VIII. REPORTS ISSUED

D. Weinstein and F. C. Holtz, "Improved Zirconium Alloys", ARF 2198-26, Summary Progress Report, U.S./EURATOM Program, February 28, 1962.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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Tech Rev - CRS

TABLE I

CORROSION BEHAVIOR OF TERNARY ZIRCONIUM ALLOYS IN 680°F WATER

Composition, w/o	Weight Gain, mg/dm^2			
	336 hr	953 hr	2040 hr	3005 hr
Zircaloy-2	18.99	23.47	29.45	43.71
Zr-1Cr-1Sb	17.40	24.56	37.87	--
Zr-1Cr-1Sb	14.84	23.19	35.24	43.59
Zr-1Cr-0.5Nb	15.13	22.18	37.31	44.37
Zr-1Cr-0.5Nb	15.81	23.71	38.39	--
Zr-1Cr-0.5Sn	16.05	21.07	32.10	32.10
Zr-1Cr-0.25Cu	20.04	25.06	35.07	36.08
Zr-1Cr-0.25Fe	13.47	17.95	30.29	--
Zr-1Cr-0.25Fe	12.80	17.72	28.56	29.54
Zr-1Cr-0.25Mo	24.30	29.16	40.83	42.77
Zr-1Cr-0.25Te	16.36	21.48	34.77	33.75
Zr-1Cr-0.25Ge	15.40	19.80	34.10	34.10
Zr-1Sb-0.5Nb	16.36	22.50	36.81	--
Zr-1Sb-0.5Nb	15.83	21.10	35.88	42.21
Zr-1Sb-0.5Sn	16.04	22.06	37.10	50.14
Zr-1Sb-0.25Cr	17.14	21.18	35.29	35.29
Zr-1Sb-0.25Cr	17.33	22.43	35.69	--
Zr-1Sb-0.25Cu	22.08	28.11	42.16	--
Zr-1Sb-0.25Fe	18.97	26.96	35.94	--
Zr-1Sb-0.25Fe	19.02	26.03	34.04	39.04
Zr-1Sb-0.25Mo	19.33	29.50	90.54	--
Zr-1Sb-0.25Mo	18.37	29.60	69.40	--
Zr-1Sb-0.25Te	19.86	26.82	36.75	40.72
Zr-1Sb-0.25Ge	15.37	21.14	29.79	34.59

TABLE I (continued)

Composition, w/o	Weight Gain, mg/dm² 336 hr	953 hr	2040 hr	3005 hr
Zr-5Sn-0.5Nb	18.24	25.33	70.93	--
Zr-5Sn-0.5Nb	19.01	25.02	72.05	--
Zr-5Sn-1Cr	18.15	29.24	125.03	--
Zr-5Sn-1Sb	18.98	34.96	95.89	--
Zr-5Sn-2.5Sb	28.26	84.78	197.81	--
Zr-5Sn-0.25Cr	17.20	22.26	67.78	--
Zr-5Sn-0.25Cu	21.31	55.80	152.18	--
Zr-5Sn-0.25Fe	25.60	43.01	100.34	--
Zr-5Sn-0.25Fe	24.57	41.28	100.24	--
Zr-5Sn-0.25Mo	21.93	69.97	173.36	--
Zr-5Sn-0.25Te	19.05	26.07	92.25	--
Zr-5Sn-0.25Ge	18.83	29.73	108.00	--
Zr-2.5Sb-1Cr	21.24	30.34	43.48	--
Zr-2.5Sb-1Cr	13.07	21.12	37.20	68.37
Zr-2.5Sb-0.5Nb	20.49	31.75	49.16	--
Zr-2.5Sb-0.5Nb	22.39	31.55	46.81	--
Zr-2.5Sb-0.5Sn	20.15	28.21	41.31	69.52
Zr-2.5Sb-1.5Sn	18.75	26.65	59.22	--
Zr-2.5Sb-1.5Sn	15.89	24.83	51.64	--
Zr-2.5Sb-0.25Cr	19.77	29.66	39.54	64.26
Zr-2.5Sb-0.25Cu	22.67	31.95	46.38	--
Zr-2.5Sb-0.25Fe	28.51	46.84	78.40	--
Zr-2.5Sb-0.25Mo	29.04	79.87	181.52	--
Zr-2.5Sb-0.25Te	24.23	35.34	52.50	--
Zr-2.5Sb-0.25Ge	20.33	30.49	50.81	--

TABLE I (continued)

Composition, w/o	Weight Gain, mg/dm^2 336 hr	953 hr	2040 hr	3005 hr
Zr-0.5Nb-0.25Cr	14.13	22.21	28.27	36.35
Zr-0.5Nb-0.25Cr	15.05	23.08	29.10	--
Zr-0.5Nb-0.25Cu	19.19	28.28	35.34	42.41
Zr-0.5Nb-0.25Fe	15.40	22.58	27.71	32.84
Zr-0.5Nb-0.25Fe	14.89	22.83	27.79	--
Zr-0.5Nb-0.25Mo	26.99	45.98	61.97	--
Zr-0.5Nb-0.25Mo	24.01	40.01	53.01	--
Zr-0.5Nb-0.25Te	14.27	24.46	30.57	40.77
Zr-0.5Nb-0.25Ge	17.00	28.00	36.00	46.00
Zr-0.5Sn-0.25Cr	14.36	21.53	25.63	30.76
Zr-0.5Sn-0.25Cr	14.39	22.14	25.46	--
Zr-0.5Sn-0.25Cu	20.53	35.61	47.82	--
Zr-0.5Sn-0.25Fe	19.29	32.49	40.61	47.71
Zr-0.5Sn-0.25Mo	16.32	26.52	35.71	63.25
Zr-0.5Sn-0.25Te	12.54	19.85	25.08	30.30
Zr-0.5Sn-0.25Ge	12.33	21.57	25.68	30.82

TABLE II

CORROSION BEHAVIOR OF TERNARY ZIRCONIUM ALLOYS IN 750° F STEAM

Composition, w/o	Weight Gain, mg/dm^2 336 hr	672 hr	1272 hr
Zircaloy-2	21.00	30.24	51.56
Zr-1Sb-0.5Nb	21.47	34.36	81.60
Zr-1Sb-0.5Nb	22.61	33.34	70.00
Zr-1Sb-0.25Cr	23.29	44.35	76.51
Zr-1Sb-0.25Cr	24.56	45.77	81.48
Zr-1Sb-0.25Mo	25.27	76.85	--
Zr-1Sb-0.25Mo	24.88	72.55	--
Zr-1Sb-0.25Te	29.13	38.83	54.21
Zr-0.5Nb-0.25Cr	16.77	27.25	37.73
Zr-0.5Nb-0.25Cr	18.49	28.76	39.03
Zr-0.5Nb-0.25Mo	26.53	42.45	60.49
Zr-0.5Nb-0.25Mo	25.20	38.84	57.74
Zr-0.5Nb-0.25Te	20.29	31.44	42.60
Zr-3Cr-1V	229.02	--	--
Zr-3Cr-1V	spalling	--	--
Zr-3Cr-1Fe	19.43	28.63	36.81
Zr-3Cr-1Sb	25.96	30.11	86.18
Zr-3Cr-0.5Nb	30.69	53.98	125.95
Zr-3Cr-0.5Nb	28.35	47.25	104.99
Zr-3Cr-0.25Mo	29.92	105.23	--
Zr-3Cr-0.25Mo	51.73	--	--
Zr-3Cr-0.25Te	18.09	26.60	36.18

TABLE II (continued)

Composition, w/o	Weight Gain, mg/dm^2 336 hr	672 hr	1272 hr
Zr-1V-1Fe	18.51	28.80	40.11
Zr-1V-1Sb	33.24	--	--
Zr-1V-0.5Nb	spalling	--	--
Zr-1V-0.5Nb	spalling	--	--
Zr-1V-0.25Cr	41.86	--	--
Zr-1V-0.25Te	34.77	--	--
Zr-1V-0.25Mo	21.64	31.94	71.10
Zr-1V-0.25Mo	23.75	38.21	76.42
Zr-1Fe-1Sb	29.14	41.62	53.07
Zr-1Fe-0.5Nb	26.48	39.72	55.00
Zr-1Fe-0.25Cr	19.30	27.43	36.57
Zr-1Fe-0.25Mo	43.03	--	--
Zr-1Fe-0.25Te	25.69	39.04	51.37

TABLE III

CORROSION BEHAVIOR OF G. N. E. C. BINARY ZIRCONIUM ALLOYS IN 680°F WATER

Composition	Weight Gain, mg/dm² 41 hr	336 hr
Zircaloy-2	9.32	14.91
Zr-0.5Cr	5.88	10.92
Zr-0.25Be	8.41	23.55
Zr-0.5Be	6.86	14.57
Zr-1.0Be	7.75	18.08
Zr-0.5Y	128.71	--
Zr-1.0Y	spalling	--
Zr-2.0Y	spalling	--
Zr-1.0Nb	6.98	16.58
Zr-15.0Nb	29.55	--
Zr-0.1Ag	76.92	--
Zr-0.5Ag	175	--
Zr-0.5V	120	--
Zr-2.0V	spalling	--
Zr-0.1Mn	110	--
Zr-0.5Mn	400	--
Zr-1.0Mn	spalling	--
Zr-0.02Pd	12.49	19.98
Zr-0.1Ba	28.78	spalling
Zr-0.5Ba	70	--
Zr-0.1Te	4.67	10.89
Zr-0.5Te	13.11	26.22
Zr-0.1Ce	11.27	21.73
Zr-0.5Ce	21.03	50.46

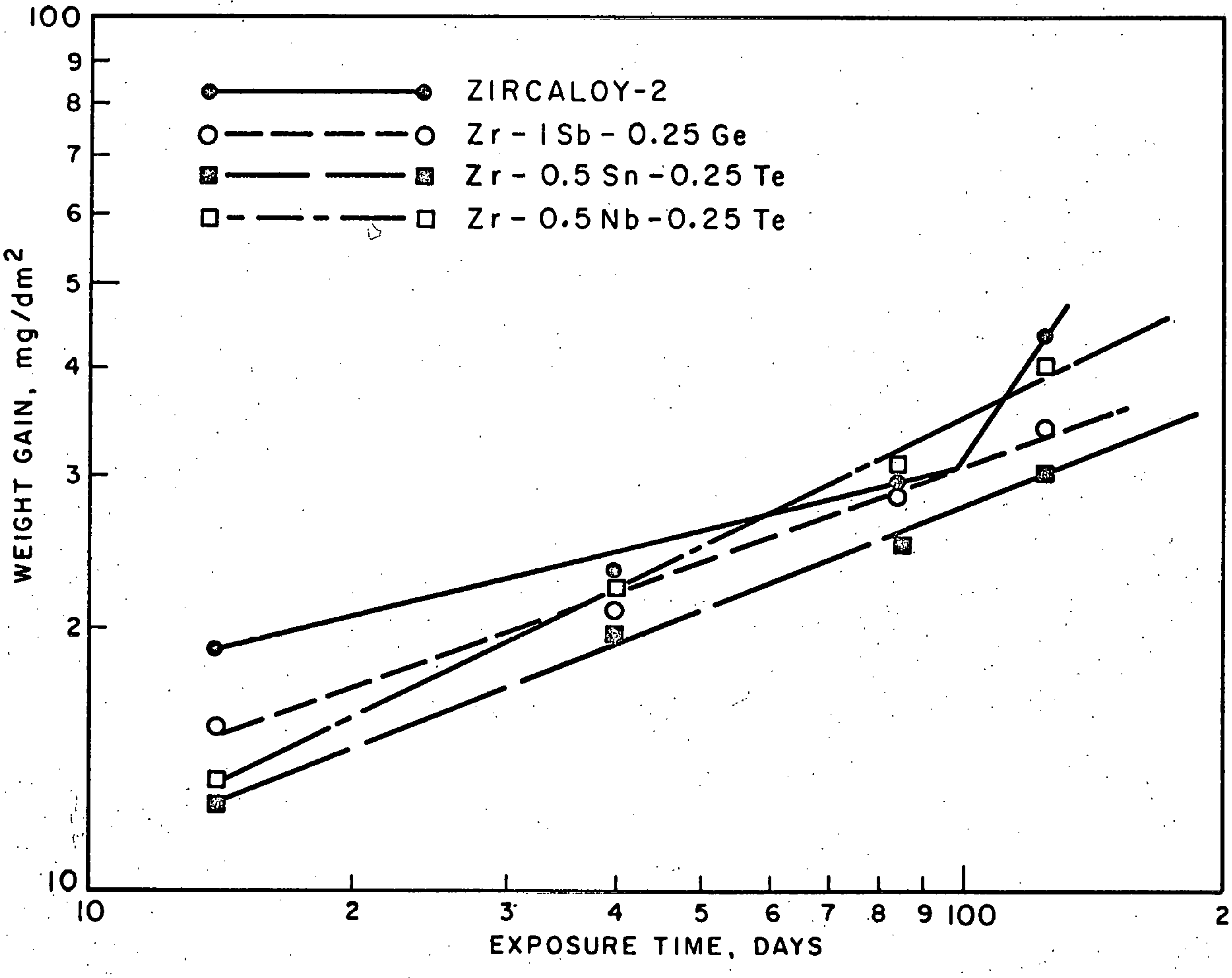

FIG. 1 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 680°F WATER.

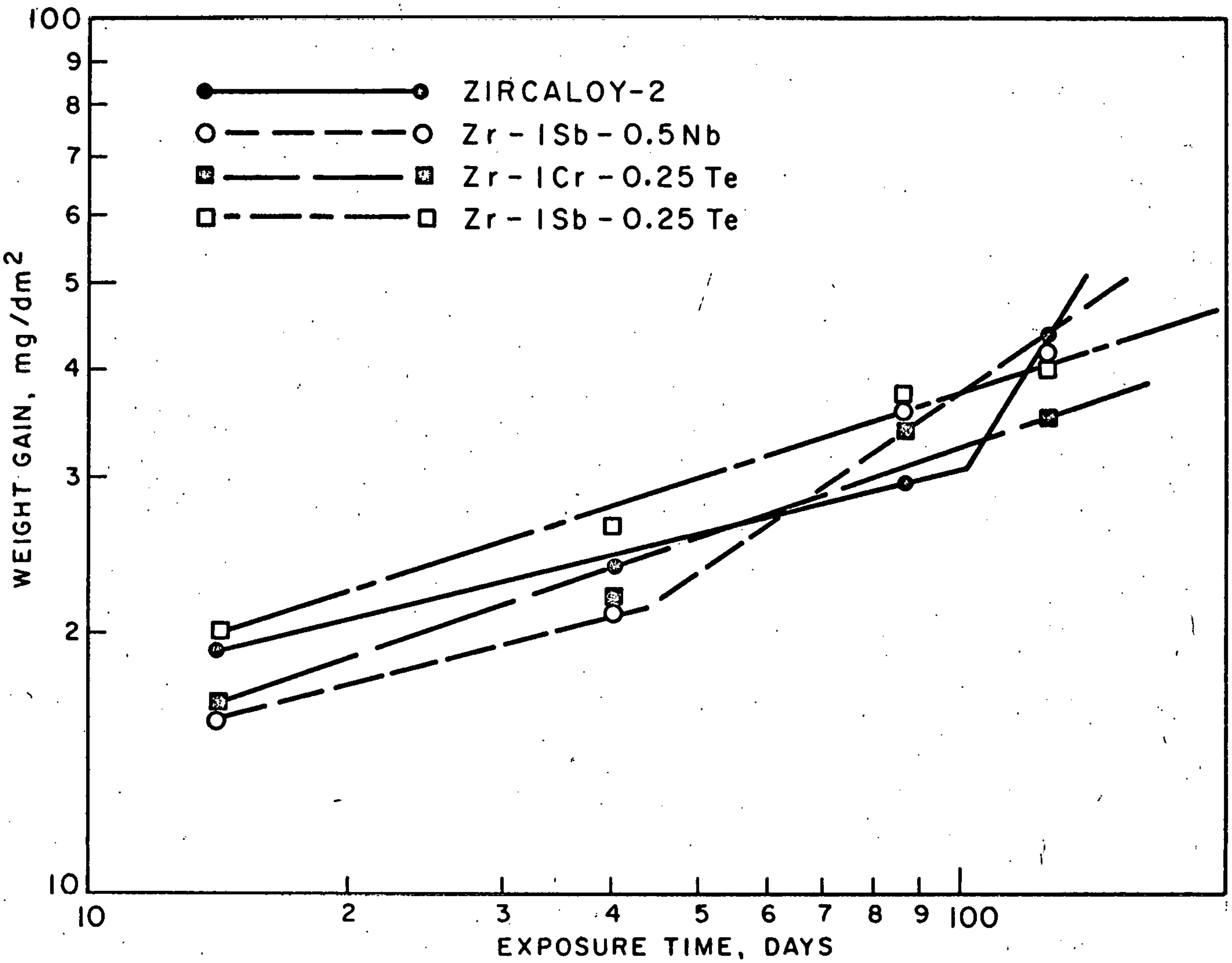

FIG. 2 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 680°F WATER.