ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

IMPROVED ZIRCONIUM ALLOYS

D. Weinstein
F. C. Holtz

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DISCLAIMER

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 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

On the basis of 4800 hours' exposure to 680°F water, a number of ternary compositions were shown to have corrosion resistance superior to Zircaloy-2. In addition, the strength and hydrogen pickup properties of these alloys were generally improved over Zircaloy-2. These promising alloys were based on the binary materials Zr-1Sb, Zr-1Cr, Zr-0.5Nb, and Zr-0.5Sn to which small percentages of Te, Ge, Cr, or Fe were added. Since our development approach has been one of choosing the most promising alloys and making modifications of these for further enhancement of properties, additional ternary materials were prepared for evaluation during the current year of work. At present, 680°F water corrosion data for an exposure time of 5000 hours are available for these modified ternary alloys.

Development of materials for potential service in 750 and 900°F steam have proceeded in a manner similar to that for 680°F water application. On the basis of corrosion resistance and strength, the alloys Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe were considered highly promising and initially acceptable. However, hydrogen pickup properties, which were about the same as Zircaloy-2, were judged as unacceptable. In an attempt to improve this latter characteristic as well as to further enhance corrosion resistance and strength, an additional series of ternary alloys was prepared; these materials are presently being evaluated for corrosion resistance to 750°F steam. The compositions studied in 900°F steam did not exhibit satisfactory corrosion resistance. Nevertheless, certain alloying additions were beneficial, and another group of alloys has been prepared for study in this atmosphere.

To study further the properties of alloys for 680°F water and 750°F steam application, 10-pound ingots of these materials were prepared by consumable arc-melting. Of particular interest will be the effect of heat treatment on corrosion resistance as well as a study of mechanical properties and fabricability. In general, these ingots will be used for a detailed property evaluation of promising ternary alloys.

III. PRINCIPAL INVESTIGATORS

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

IV. STATEMENT OF PROBLEM

The program objectives are development of zirconium-base alloys having corrosion resistance, strength, and hydrogen pickup properties superior to Zircaloy-2 in 680°F water; another, more difficult, objective is the development of zirconium alloys, for cladding and other in-core applications, which are corrosion resistant to 750 and 900°F steam and possess the required strength and hydrogen-uptake properties in this environment.

V. DESCRIPTION OF WORK--RESULTS

Based on corrosion data of last year, modified ternary alloys have been exposed to 680°F water (2700 psi) for a period of 213 days (5016 hours). Weight gain data have been obtained at various times, and these results are given in Table I. In addition, log weight gain versus log time curves of the best alloy from each group of compositions are presented in Figure 1 and Figure 2, and a linear coordinate plot of weight gain versus exposure time for two of these alloys is shown in Figure 3. Curves for corrosion of Zircaloy-2 are given for comparison.

Examination of the corrosion behavior of various groups of compositions (Table I) shows that, in general, there is little significant change in pretransition corrosion resistance, with minor variations in alloying concentration. For example, in the Zr-Sn-Te group, most alloys exhibit a weight gain of 50 to 55 mg/dm^2 after 213 days' exposure. In this group, the alloy Zr-0.5Sn-0.3Te shows the lowest weight gain; however, it is not significantly lower than most of the other values. The markedly higher value for the alloy with only 0.1 wt% more tellurium appears unrealistic in view of the similarity of values between alloys having much wider compositional variation. The corrosion curve of Zr-0.5Sn-0.3Te is shown in Figure 1; comparing its behavior to that of Zircaloy-2, there is little real advantage, from a corrosion standpoint, in using this material. Although the initial corrosion rate is lower than Zircaloy-2 and transition occurs somewhat later, the post-transition corrosion rate(the most important consideration in evaluation of corrosion properties) is essentially equivalent to Zircaloy-2. This alloy and the other Zr-Sn-Te materials were based on the properties obtained for Zr-0.5Sn-0.25Te during last year; one may conclude that there is no significant difference in corrosion properties.

The best corrosion behavior was exhibited by alloys within the Zr-Cr-Te and Zr-Nb-Te groups (Table I); in particular, the materials Zr-0.75Cr-0.4Te and Zr-0.5Nb-0.4Te showed outstanding corrosion properties, as shown in Figure 1. Up to the total exposure time, there is no evidence of transition to linear, accelerated corrosion. To show the

TABLE I

CORROSION PROPERTIES OF TERNARY ALLOYS IN 680°F WATER

Composition, wt%	Weight Gain, mg/dm^2 14 days	42 days	84 days	125 days	167 days	213 days
Zircaloy-2	16.53	22.94	28.01	45.93	61.12	75.33
Zr-0.4Sn-0.4Te	14.34	18.56	26.15	30.37	48.93	54.84
Zr-0.5Sn-0.5Te	15.46	22.79	30.11	35.00	46.39	52.90
Zr-0.5Sn-0.3Te	12.94	18.60	24.26	29.11	46.10	50.14
Zr-0.5Sn-0.4Te	15.75	22.38	31.50	48.08	62.17	68.80
Zr-0.6Sn-0.3Te	13.95	20.93	26.35	32.55	48.05	53.48
Zr-0.75Sn-0.25Te	15.71	21.82	27.05	35.75	52.36	55.85
Zr-0.75Sn-0.4Te	14.56	21.45	27.58	34.48	50.57	55.17
Zr-0.9Sn-0.35Te	13.96	19.70	25.45	35.30	55.01	63.21
Zr-0.5Sn-0.3Ge	14.19	20.49	25.22	31.53	45.71	56.75
Zr-0.5Sn-0.4Ge	14.02	20.25	26.48	35.05	55.31	61.54
Zr-0.75Sn-0.25Ge	14.62	23.08	30.01	41.55	72.32	84.63
Zr-0.75Sn-0.4Ge	15.07	21.86	27.13	33.16	53.51	61.05
Zr-0.9Sn-0.35Ge	15.56	22.24	27.42	38.54	62.26	68.93
Zr-0.75Sb-0.25Ge	17.32	28.34	37.00	41.73	54.33	59.05
Zr-0.75Sb-0.4Ge	18.73	28.50	37.45	44.78	56.18	70.02
Zr-1Sb-0.2Ge	19.93	29.06	37.37	53.15	61.45	61.45
Zr-1Sb-0.4Ge	19.65	30.29	35.20	48.30	66.31	74.50

TABLE I (continued)

Composition, wt%	Weight Gain, mg/dm^2					
	14 days	42 days	84 days	125 days	167 days	213 days
Zr-1.2Sb-0.25Ge	19.78	30.06	37.18	52.21	52.21	51.42
Zr-1.2Sb-0.4Ge	20.66	32.22	50.40	--	--	--
Zr-1.5Sb-0.2Ge	20.41	31.06	39.93	56.79	56.79	56.79
Zr-0.3Nb-0.5Te	14.84	22.69	32.30	40.15	48.88	49.75
Zr-0.4Nb-0.25Te	14.08	23.18	30.64	37.26	43.06	47.20
Zr-0.4Nb-0.4Te	43.19(crack)	--	--	--	--	--
Zr-0.5Nb-0.3Te	16.91	25.77	35.44	43.49	49.94	55.58
Zr-0.5Nb-0.4Te	15.62	21.87	30.46	36.71	42.96	46.08
Zr-0.75Nb-0.25Te	18.63	31.05	43.47	54.34	62.10	71.41
Zr-0.75Nb-0.4Te	18.47	31.55	43.86	53.87	66.18	81.57
Zr-0.75Sb-0.2Te	16.97	23.91	30.85	47.82	64.79	77.90
Zr-0.75Sb-0.3Te	18.41	26.21	35.41	53.83	70.12	89.24
Zr-0.75Sb-0.4Te	18.53	27.39	37.06	43.50	54.78	69.28
Zr-1Sb-0.2Te	15.55	23.32	30.32	38.87	55.20	66.09
Zr-1Sb-0.4Te	18.12	29.65	39.53	47.77	63.42	79.07
Zr-1.2Sb-0.15Te	24.29	35.56	--	--	--	--
Zr-0.75Sb-0.4Nb	14.97	21.27	27.57	32.30	55.15	63.03
Zr-0.75Sb-0.5Nb	15.52	22.18	28.09	34.01	56.18	66.53
Zr-1Sb-0.35Nb	16.23	23.97	30.15	50.25	65.71	85.81

TABLE I (continued)

Composition, wt%	Weight Gain, mg/dm^2					
	14 days	42 days	84 days	125 days	167 days	213 days
Zr-0.75Cr-0.4Te	13.35	19.19	23.37	26.71	30.04	33.38
Zr-0.75Cr-0.5Te	13.27	19.91	25.71	29.03	34.01	36.49
Zr-0.85Cr-0.25Te	12.92	19.00	24.32	27.36	32.68	35.72

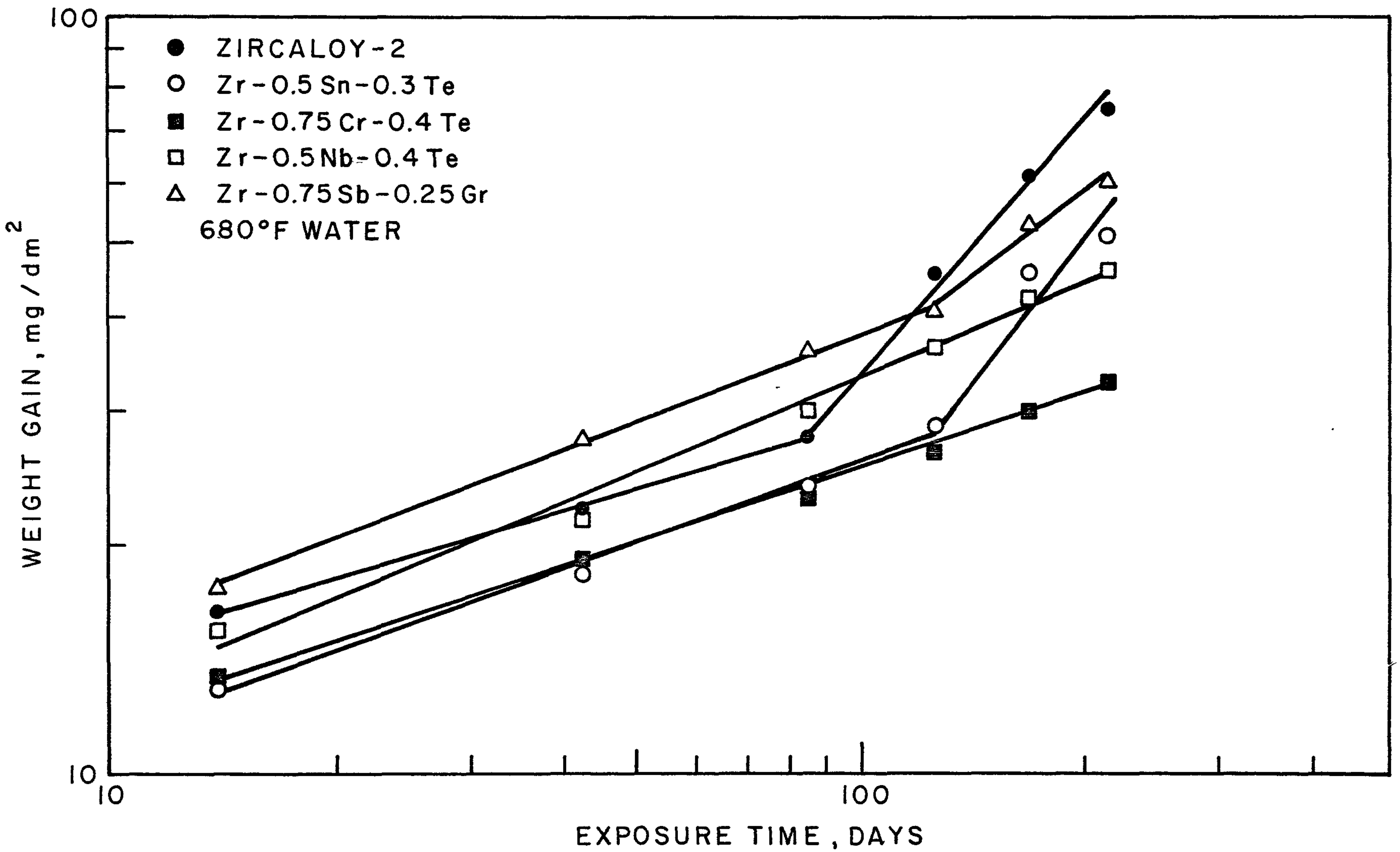

FIG. 1 - CORROSION OF TERNARY ZIRCONIUM ALLOYS IN 680° F WATER

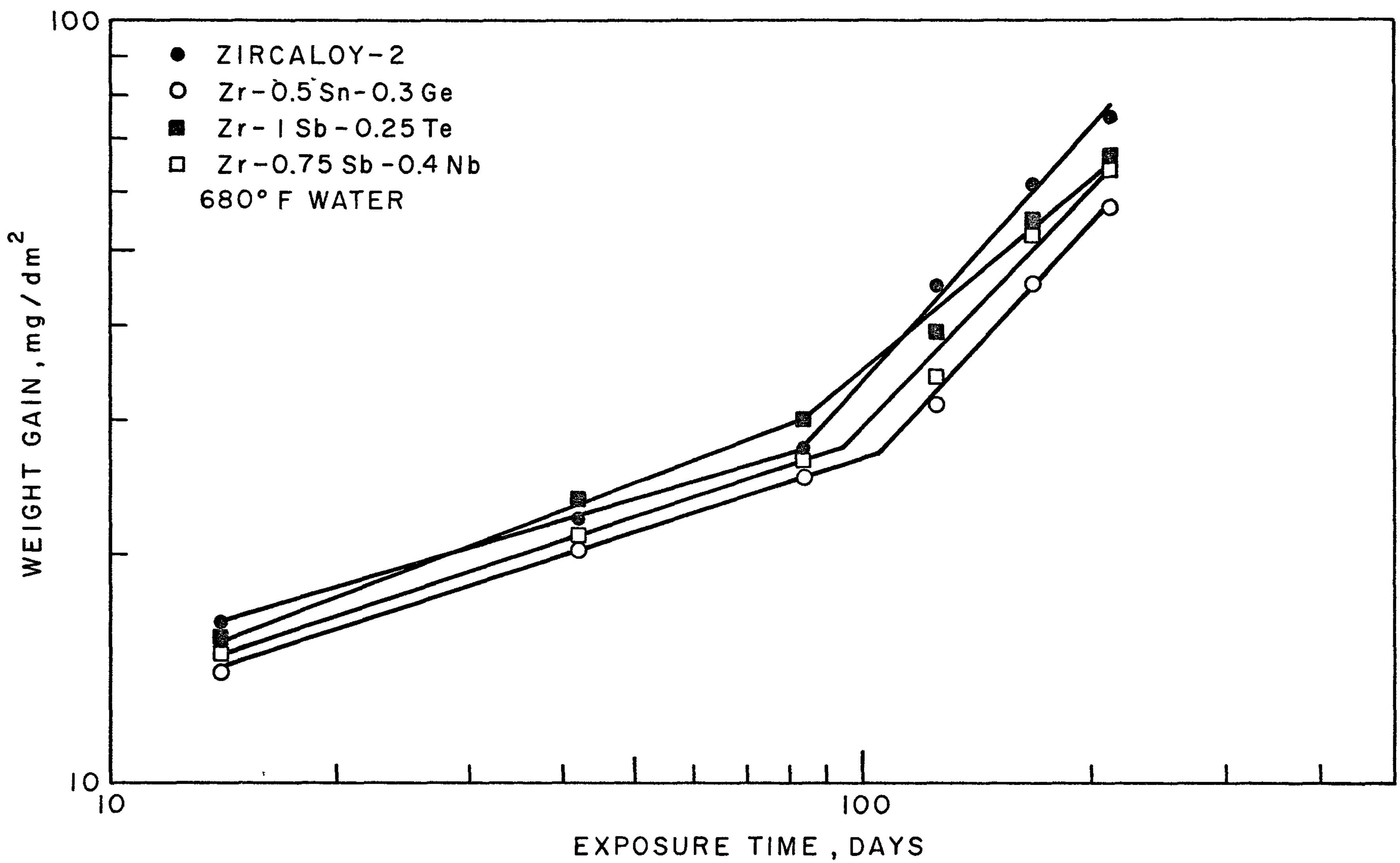

FIG. 2 - CORROSION OF TERNARY ZIRCONIUM ALLOYS IN 680°F WATER

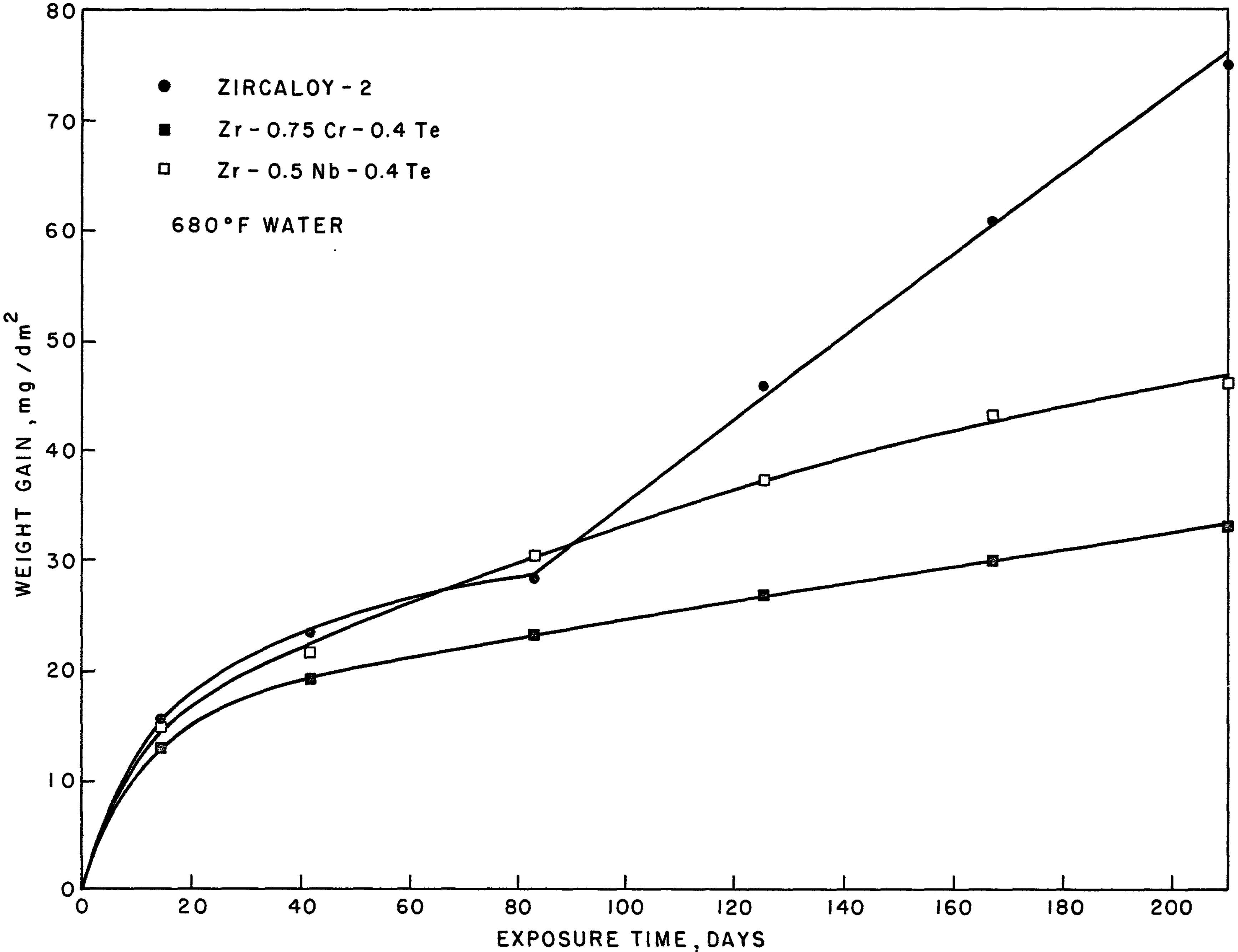

FIG. 3 - CORROSION OF TERNARY ZIRCONIUM ALLOYS IN 680°F WATER

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parabolic or pseudo-parabolic nature of the rate of corrosion, a linear coordinate plot of data for these alloys is shown in Figure 3. Such corrosion behavior represents a significant improvement over Zircaloy-2 which, in these tests, underwent transition to linear corrosion at about 85 days of exposure. One should note, however, that Zr-1Cr-0.25Te and Zr-0.5Nb-0.25Te, materials that were evaluated last year, also did not exhibit "breakaway" corrosion. In fact, comparison of weight gains shows that no significant change in corrosion properties was obtained with small variation of alloying element concentration. Although mechanical properties and hydrogen pickup have not yet been determined, results obtained last year indicate that Zr-0.75Cr-0.4Te and Zr-0.5Nb-0.4Te will be superior to Zircaloy-2 in these parameters. The previously reported strength properties, at least, are primarily due to the potent effect of tellurium as a hardener of zirconium. The improvement in corrosion-hydrogen uptake is probably due to the absence of nickel, which is an addition to Zircaloy-2, and to the fact that tellurium, chromium, and niobium, particularly the latter, as binary alloying elements in zirconium do not result in high hydrogen pickup.

The remaining groups of alloys (Table I) all exhibit breakaway corrosion at times roughly equivalent to Zircaloy-2. The best alloy of each group, in terms of weight gain, is shown in Figures 1 and 2. Generally, the post-transition corrosion rate is not markedly different from Zircaloy-2, and aside from strength and hydrogen pickup properties, there is no particular advantage in using these materials rather than Zircaloy-2. One should note also that little significant change in corrosion properties was noted from the original ternary compositions studied last year.

Although the neutron absorption cross section of experimental alloys has not been determined, and a comparison with Zircaloy-2 is therefore not possible, another approach has been used by H. H. Klepfer, VAL, for determining acceptability of alloys on the basis of neutron economy. In his program entitled "Design of Specific Zirconium Alloys" (EURATOM), Klepfer calculates the maximum tolerable alloy concentration of various elements in the cladding such that the additional U^{235} enrichment of natural uranium in the Dresden Reactor (boiling water) core shall not exceed 0.02 to 0.05 per cent. His alloy design then must not exceed these specifications. From Klepfer's data, the Zr-0.75Cr-0.4Te and the Zr-0.5Nb-0.4Te alloys, as well as most of the other promising experimental compositions in this program, fall within the above neutron economy or fuel enrichment requirements.

Study of corrosion behavior in 750° F steam (1500 psi) of experimental ternary compositions has been initiated; however, the available data are for exposure times too short to make valid conclusions. Again, these materials (Table II) were prepared on the basis of the most promising alloys studied last year. Many of these compositions did not exhibit transition-corrosion behavior up to 125 days; however, the major problem was the pickup of rather large amounts of corrosion-hydrogen. Hopefully, this property will be improved somewhat in the alloys presently being studied.

Compositions for evaluation in 900° F steam (refreshed system) have been arc-melted and are presently being fabricated into corrosion specimens. The alloys prepared, which follow from the results of last year's study, are presented in Table III. Corrosion as well as hydrogen pickup is rather severe in this atmosphere.

The alloy studies thus far performed have employed materials in the as-fabricated condition. While certain properties have been satisfactory, it is well known that heat treatment could further improve alloy characteristics. Additional data on strength and hydrogen pickup as well as impact data and hydrogen embrittlement information on promising alloys are necessary. As a result, relatively large ingots (10 pounds) of certain acceptable alloys for 680° F water and 750° F steam application have been prepared by consumable arc-melting. The materials thus far produced are Zr-0.5Nb-0.25Te, Zr-1Cr-0.25Te, Zr-1V-1Fe, Zr-3Cr-1Fe, and Zr-3Cr-0.25Te; the first two alloys are for water application, and the last three are for steam. These ingots have been surface conditioned and will be fabricated by press-forging to 1-inch thick plate at approximately 1700° F

TABLE II

ALLOYS STUDIED IN 750° F STEAM

Zr-0.75Fe-0.5Cr	Zr-4Cr-0.6Te
Zr-1Fe-0.5Cr	Zr-4Cr-1Te
Zr-1Fe-1Cr	Zr-5Cr-0.8Te
Zr-1.5Fe-0.25Cr	
Zr-1.5Fe-1Cr	Zr-0.75V-0.75Fe
Zr-1.5Fe-1.5Cr	Zr-1V-0.5Fe
Zr-2Fe-1.5Cr	Zr-1V-0.75Fe
	Zr-1.25V-0.75Fe
Zr-2Cr-0.75Fe	Zr-1.25V-1.25Fe
Zr-2.5Cr-0.75Fe	Zr-1.5V-1Fe
Zr-3Cr-0.5Fe	Zr-1.5V-1.5Fe
Zr-3Cr-1.5Fe	Zr-1.75V-1.75Fe
Zr-3.5Cr-0.5Fe	Zr-2V-1Fe
Zr-3.5Cr-1Fe	Zr-2V-2Fe
Zr-3.5Cr-1.5Fe	
Zr-4Cr-1Fe	Zr-0.8Fe-0.3Te
	Zr-0.7Fe-0.5Te
Zr-0.5Nb-0.35Te	Zr-1.2Fe-0.7Te
Zr-0.4Nb-0.35Te	
Zr-0.7Nb-0.5Te	Zr-0.75Sb-1Fe
Zr-0.9Nb-0.5Te	Zr-1Sb-0.75Fe
	Zr-1Sb-1.5Fe
Zr-2.5Cr-0.25Te	Zr-1Sb-2Fe
Zr-2.5Cr-0.5Te	Zr-1.5Sb-1Fe
Zr-3Cr-0.4Te	Zr-1.5Sb-1.5Fe
Zr-3Cr-0.7Te	
Zr-3Cr-1Te	Zr-0.5Nb-0.5Cr
Zr-3Cr-1.5Te	Zr-0.75Nb-0.5Cr
Zr-3.5Cr-0.5Te	Zr-0.75Nb-0.5Cr

TABLE III

ALLOYS STUDIED IN 900°F STEAM

Zr-0.5Nb-0.1Mo	Zr-3Cr-0.25Te
Zr-0.5Nb-0.4Mo	Zr-3Cr-0.5Te
Zr-0.4Nb-0.25Mo	
Zr-0.75Nb-0.25Mo	Zr-3Cr-1Fe
	Zr-3Cr-3Fe
Zr-0.5Nb-0.25Te	
	Zr-3Cr-0.25Sb
Zr-1V-0.15Mo	Zr-3Cr-0.5Sb
Zr-1V-0.5Mo	Zr-3Cr-1Sb
Zr-0.75V-0.25Mo	
Zr-1.5V-0.25Mo	Zr-1Mo-0.25Te
Zr-2V-0.25Mo	Zr-1Mo-0.25Sb
	Zr-1Mo-1Fe
Zr-1V-0.25Te	
Zr-1V-0.5Te	Zr-4Fe
	Zr-5Fe
Zr-3Cr-0.25Nb	Zr-2Cr
	Zr-4Cr
	Zr-6Cr

followed by hot-rolling to sheet about 1550° F. From this material, numerous tensile, impact, and corrosion specimens will be prepared and evaluated using various heat treatment techniques.

VI. FUTURE WORK

Alloys presently being evaluated in 680° F water will be exposed for 250 days (6000 hours). At that time, final weight gain measurements will be obtained, and the amount of absorbed hydrogen will be determined (specimen destroyed). However, the Zr-Cr-Te and Zr-Nb-Te alloys which have not yet exhibited breakaway will be exposed until the transition point and post-transition corrosion rate are defined. These parameters must be known if these materials are to be employed in reactor service. For compositions showing acceptable corrosion and hydrogen pickup properties, tensile data at elevated temperatures will be obtained. At this point, it is necessary to decide on the value of these alloys compared to the properties obtained for compositions now available in large ingots. From the data available at this time, it would seem that the present alloys are essentially equivalent to those now being evaluated, at least in terms of corrosion resistance. There is a good possibility that enhanced strength will be shown by the modified ternary alloys, due primarily to the increased tellurium contents, and additional consumable arc-melted ingots can be prepared and evaluated during the current year.

Studies of alloys in 750° and 900° F steam will be carried out during the next quarter, and major emphasis in alloy development will be shifted to these atmospheres. Three consumably melted ingots of materials for 750° F steam service will be fabricated and studied in detail. As corrosion data become available on the modified ternary series, additional promising alloys may be indicated for further study or modification. In 900° F steam, the corrosion properties of the present series of alloys must be determined. For the longer range, the experimental effort should be entirely shifted to studies in steam 750° F and higher; by the end of the current year, evaluation of alloys for 680° F water will be completed. Also at that time, a number of highly promising alloys should be available for potential steam application, and further work should be limited to detailed study of these materials.

VII. CONCLUSIONS

A number of ternary alloys have been developed for service in 680° F water which meet the objectives of this program on the basis of corrosion resistance, strength, and hydrogen pickup. In particular, these materials are based on Zr-Cr and Zr-Nb with small additions of Te. Initial studies on ternary alloys in 750° F steam indicate that some materials are acceptable on the basis of corrosion resistance and strength; these are Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe. However, hydrogen pickup during corrosion is excessively high. Additional materials are being evaluated for the purpose of enhancing properties. For 900° F steam, no material has yet been judged acceptable for potential service in this medium; additional work is being carried out on this development.

VIII. REPORTS ISSUED

D. Weinstein and F. C Holtz, "Development of Improved Zirconium Alloys for Use in Superheated Water and Steam," Proceedings, USAEC Symposium on Zr Alloy Development, GEAP-4089, Vol. 6, November 1962.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

D. Weinstein
Research Metallurgist
Metals and Ceramics Research

F. C. Holtz
Senior Metallurgist
Metals and Ceramics Research

DW/rh

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