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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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

Before the beginning of the current year of investigation, a number of ternary alloys had been developed which exhibited promising corrosion properties in 680°F water or 750°F steam. In the case of alloys for superheated water service, corrosion resistance, strength, and hydrogen pickup were superior to Zircaloy-2. It was apparent that the investigation should proceed in a manner designed to determine the concentration of alloying elements which would result in an optimum combination of these properties. Therefore at the beginning of the current year, minor compositional modifications were made. At present, corrosion data in 680°F water are available for an exposure time of approximately 7000 hours, and tensile properties at room and elevated temperature have been determined. On the basis of these data and the anticipated values of hydrogen pickup, alloys having the nominal compositions Zr-0.75Cr-0.4Te and Zr-0.5Nb-0.4Te represent a notable improvement over Zircaloy-2.

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Development of an acceptable zirconium alloy for application in 750° F steam has proceeded in a similar manner during the current year. We had determined, on the basis of 3000-hour exposure to 750° F static steam, that the compositions Zr-3Cr-1Fe, Zr-3Cr-0.25Te, Zr-1V-1Fe, and Zr-0.5Nb-0.25Te exhibited reasonable corrosion resistance to this medium. Like Zircaloy-2, however, the pickup of corrosion hydrogen by these alloys was excessive, and although time to transition and post-transition corrosion rate were improved over Zircaloy-2, resistance to this atmosphere was judged inadequate. Modifications of these materials have been made by varying alloy concentrations, particularly for the system Zr-Cr-Fe, and 750° F steam exposure is now in progress.

Development of a truly acceptable zirconium alloy for use in 900° F steam has not yet been realized in this program or any past investigations. The literature is replete with data on a large number of alloys showing very high corrosion rates, substantial absorption of corrosion hydrogen, or marginal strength. Nevertheless, more recent work at various laboratories indicates that such a development is within the realm of possibility; in some cases, at least, a substantial departure from the common, low alloying concentration levels to zirconium has yielded rather promising results. We have determined that relatively high concentrations of chromium, iron, vanadium, or molybdenum improve the corrosion resistance of zirconium to 900° F steam. Various ternary alloys of these elements with zirconium have shown some encouraging corrosion results. At present, an additional group of ternary materials are being evaluated in this medium.

As previously brought out, near the beginning of the current year of work, a number of alloys were considered initially acceptable for use in 680° F water. Although further modification of alloy concentration was planned, it was equally necessary that more detailed knowledge of properties of these alloys be known. Such work has been performed concurrently with corrosion studies during the current year. Consumable arc-melted ingots (10-pound starting charge) have been prepared and fabricated to sheet; investigations of heat-treatment effects on corrosion and strength properties are now in progress.

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 objective is 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

The results of corrosion evaluation of ternary alloys in 680° F water for an exposure time to 292 days (7000 hours) are presented in Table I. As previously discussed in Quarterly Report ARF-B198-39, alloys within the systems Zr-Nb-Te and Zr-Cr-Te exhibited the best corrosion properties of this group. Moreover, inspection of these data show that certain alloys, within the above two systems, have markedly improved corrosion resistance over Zircaloy-2. For example, the corrosion behavior of the alloys Zr-0.5Nb-0.4Te and Zr-0.75Cr-0.4Te is plotted in Figure 1 and Figure 2, along with that determined for Zircaloy-2. The latter material showed breakaway corrosion at a weight gain of about 28 mg/dm² and after an exposure time of approximately 85 days. Compared to published data of Bettis Atomic Power Laboratory, the time value is slightly low; however, the rates of corrosion following transition agree very well. As shown in Figure 1, the experimental alloys exhibit a significantly longer time to transition and a lower post-transition corrosion rate; for the Zr-0.75Cr-0.4Te alloy, this rate is a factor of two lower than for Zircaloy-2. In fact, the transition is rather poorly defined for the Zr-0.75Cr-0.4Te alloy and one could just as easily not show an inflection in the log-log plot. On rectangular coordinates, as shown in Figure 2, a smooth pseudo-parabolic curve can be drawn through all the data points. Thus, it is

TABLE I

CORROSION PROPERTIES OF TERNARY ALLOYS IN 680° F WATER

Composition	Weight Gain, mg/dm ²							
	14 days	42 days	84 days	125 days	167 days	213 days	250 days	292 days
Zircaloy-2	16.53	22.94	28.01	45.93	61.12	75.33	93.67	113.80
Zr-0.4Sn-0.4Te	14.34	18.56	26.15	30.37	48.93	54.84	63.27	76.77
Zr-0.5Sn-0.5Te	15.46	22.79	30.11	35.00	46.39	52.90	143.22	----
Zr-0.5Sn-0.3Te	12.94	18.60	24.26	29.11	46.10	50.14	56.61	66.32
Zr-0.5Sn-0.4Te	15.75	22.38	31.50	48.08	62.17	68.80	81.24	95.33
Zr-0.6Sn-0.3Te	13.95	20.93	26.35	32.55	48.05	53.48	58.12	67.43
Zr-0.75Sn-0.25Te	15.71	21.82	27.05	35.75	52.36	55.85	61.09	71.56
Zr-0.75Sn-0.4Te	14.56	21.45	27.58	34.48	50.57	55.17	65.13	79.69
Zr-0.9Sn-0.35Te	13.96	19.70	25.45	35.30	55.01	63.21	70.60	88.67
Zr-0.5Sn-0.3Ge	14.19	20.49	25.22	31.53	45.71	56.75	68.57	89.85
Zr-0.5Sn-0.4Ge	14.02	20.25	26.48	35.05	55.31	61.54	72.44	88.80
Zr-0.75Sn-0.25Ge	14.62	23.08	30.01	41.55	72.32	84.63	109.25	----
Zr-0.75Sn-0.4Ge	15.07	21.86	27.13	33.16	53.51	61.05	68.58	85.92
Zr-0.9Sn-0.35Ge	15.56	22.24	27.42	38.54	62.26	68.93	83.75	102.28
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	250 days	292 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	53.24	62.84
Zr-0.4Nb-0.25Te	14.08	23.18	30.64	37.26	43.06	47.20	52.99	58.79
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	62.82	72.49
Zr-0.5Nb-0.4Te	15.62	21.87	30.46	36.71	42.96	46.08	51.55	60.92
Zr-0.75Nb-0.25Te	18.63	31.05	43.47	54.34	62.10	71.41	85.39	105.57
Zr-0.75Nb-0.4Te	18.47	31.55	43.86	53.87	66.18	81.57	103.89	----
Zr-0.75Sb-0.2Te	16.97	23.91	30.85	47.82	64.79	77.90	96.41	114.15
Zr-0.75Sb-0.3Te	18.41	26.21	35.41	53.83	70.12	89.24	109.07	----
Zr-0.75Sb-0.4Te	18.53	27.39	37.06	43.50	54.78	69.28	83.78	96.67
Zr-1Sb-0.2Te	15.55	23.32	30.32	38.87	55.20	66.09	80.08	93.29
Zr-1Sb-0.4Te	18.12	29.65	39.53	47.77	63.42	79.07	93.90	----
Zr-1.2Sb-0.15Te	24.29	35.56	----	----	----	----	----	----

TABLE I (continued)

Composition, wt%	Weight Gain, mg/dm ²							
	14 days	42 days	84 days	125 days	167 days	213 days	250 days	292 days
Zr-0.75Sb-0.4Nb	14.97	21.27	27.57	32.30	55.15	63.03	78.78	96.90
Zr-0.75Sb-0.5Nb	15.52	22.18	28.09	34.01	56.18	66.53	84.27	101.27
Zr-1Sb-0.35Nb	16.23	23.97	30.15	50.25	65.71	85.81	105.91	----
Zr-0.75Cr-0.4Te	13.35	19.19	23.37	26.71	30.04	33.38	36.72	40.89
Zr-0.75Cr-0.5Te	13.27	19.91	25.71	29.03	34.01	36.49	41.47	44.79
Zr-0.85Cr-0.25Te	12.92	19.00	24.32	27.36	32.68	35.72	47.11	55.47

FIG. 1 - CORROSION BEHAVIOR OF TWO EXPERIMENTAL ZIRCONIUM ALLOYS IN 680° F WATER.

FIG. 2 - CORROSION BEHAVIOR OF TWO EXPERIMENTAL ZIRCONIUM ALLOYS IN 680°F WATER.

possible to suggest that Zr-0.75Cr-0.4Te has not yet reached transition for 292 days' exposure to 680°F water. The alloy Zr-0.5Nb-0.4Te has apparently undergone transition at about 210 days, and the transition corrosion rate is lower than that for Zircaloy-2.

In the rectangular coordinate plot of Figure 2, Zircaloy-2 corrosion is observed to go through a series of rate transitions, and the Zr-0.5Nb-0.4Te alloy appears to have entered at least the first rate transition. Such behavior for Zircaloy has been well established by Shannon and others at Hanford Atomic Products Operation. It has been suggested that these rate transitions are associated with oxide film cracking and reformation of adherent corrosion oxide. In order for this effect to be observed, therefore, corrosion weight gain data must be taken periodically on the same specimen until the test is concluded. Such was the procedure in this investigation, whereas the commonly used Bettis data, which show no rate transitions of this type, were obtained using a large number of specimens and removing one or more at various times for weight gain determinations.

The strength and ductility at room temperature and 680°F of alloys in the systems Zr-Cr-Te and Zr-Nb-Te, compared with that for Zircaloy-2, are given in Table II. These tests were performed on sheet specimens having a gage length of 0.75 inch; a 10,000-pound capacity Instron machine was used, and the load-elongation curve was recorded autographically. A crosshead speed of 0.05 inch/min was employed, and each value represents the average of two tests; specimens evaluated at elevated temperature were in a helium-filled capsule maintained at slightly positive pressure. With the exception of Zr-0.75Cr-0.5Te, room-temperature strength values are lower than Zircaloy-2. The yield stresses, which are probably more important parameters than ultimate tensile strengths, are generally slightly below that for Zircaloy-2. Total elongation at room temperature is quite satisfactory, and no difficulty was encountered during fabrication of these materials. The strength superiority of these materials over Zircaloy-2 becomes apparent at the test temperature of 680°F. The Zr-Nb-Te alloys have ultimate tensile strengths and yield stresses higher

TABLE II

TENSILE PROPERTIES OF TERNARY ZIRCONIUM ALLOYS
AT ROOM TEMPERATURE AND 680° F

Composition	Ultimate Tensile Strength, psi	Yield Stress (0.2% offset), psi	Elongation, %
<u>Room Temperature</u>			
Zircaloy-2	67,000	49,400	31.0
Zr-0.75Cr-0.4Te	58,750	41,500	28.4
Zr-0.75Cr-0.5Te	69,700	54,750	14.2
Zr-0.85Cr-0.25Te	62,050	45,750	22.7
Zr-0.3Nb-0.5Te	61,250	49,250	24.5
Zr-0.4Nb-0.25Te	59,050	46,850	25.6
Zr-0.5Nb-0.3Te	64,550	50,200	22.0
Zr-0.5Nb-0.4Te	60,650	47,500	26.9
<u>680° F</u>			
Zircaloy-2	26,800	23,170	37.7
Zr-0.75Cr-0.4Te	28,400	20,100	30.8
Zr-0.75Cr-0.5Te	37,000	26,800	18.1
Zr-0.85Cr-0.25Te	29,400	20,900	32.0
Zr-0.3Nb-0.5Te	31,900	28,750	15.6
Zr-0.4Nb-0.25Te	29,300	26,900	14.0
Zr-0.5Nb-0.3Te	35,000	26,300	18.9
Zr-0.5Nb-0.4Te	32,400	28,300	18.3

than Zircaloy-2; however, the elongation of Zr-Nb-Te alloys is noticeably reduced at this temperature. Such behavior suggests the occurrence of an aging process at 680°F. While aging phenomena have been observed in Zircaloy-2 at elevated temperatures, no work of this nature has been carried out on these experimental compositions. The improved elevated-temperature strength is in part due to the tellurium addition, which has been reported to be a strong solid-solution hardener of zirconium. In addition, all of the niobium might be in solid solution with zirconium at 680°F.

The remaining property to be determined for these alloys is the amount of hydrogen picked up during corrosion. From previous work on these alloys, this quantity should be less than for Zircaloy-2.

VI. FUTURE WORK

A group of ternary alloys are presently being evaluated in 750°F steam; meaningful corrosion data will be available during the next quarter. Ternary materials will also be evaluated in 900°F steam during the next quarter. The compositions being investigated in these media have been tabulated in the preceding Quarterly Report (ARF-B198-39).

Corrosion data for alloys in 680°F water have been carried out to 7000 hours' exposure, and the behavior of acceptable alloys has been reasonably well defined. These materials were in the as-rolled condition. In view of the fact that heat treatment can markedly change corrosion and mechanical properties, a good deal more emphasis will be placed on this aspect of the program in future work. For alloys being considered for 680°F water application, consumable arc-melted ingots of Zr-0.5Nb-0.25Te and Zr-1Cr-0.25Te have been prepared and fabricated to sheet. Corrosion and mechanical properties are to be determined for these materials in the following three conditions:

1. as-rolled
2. 950°C, 30 min --> water quenched;
age 500°C, 8 hr --> air cool.
3. 950°C, 30 min --> water quenched;
cold reduce 30 per cent by rolling;
age 500°C, 8 hr --> air cool.

One theory of zirconium corrosion relates the fineness of intermediate phase precipitates in the alpha-zirconium matrix to the degree of corrosion resistance. At 950° C these alloys will consist entirely of beta zirconium; after quenching and aging, the precipitate phases will be markedly finer than alpha/beta as-rolled material. The intermediate deformation process is intended to further reduce the size of precipitates. The latter procedure has been used successfully in improving the corrosion rate (at least in the pre-transition region) of Zircaloy-2. One might further suggest that such heat treatment might improve mechanical properties.

A detailed Summary Report of the current year of work will be issued by August 1, 1963.

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 probably hydrogen pickup. 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, Zr-0.5Nb-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

None

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

D. Weinstein
Research Metallurgist
Materials and Structures Research

F. C. Holtz
Senior Metallurgist
Materials and Structures Research

DW/rh

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