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IMPROVED ZIRCONIUM ALLOYS

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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 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

Corrosion studies were carried out on a large number of ternary alloys (prepared on the basis of corrosion data for binary compositions) in 680°F water for 4800 hours and 750°F steam for 3000 hours. On the basis of this evaluation and determination of tensile strength, a number of materials were considered highly promising and initially satisfy the program objective. For 680°F water, acceptable compositions are based on Zr-1Sb, Zr-1Cr, Zr-0.5Nb, and Zr-0.5Sn with small additions of Te, Ge, Cr, or Fe. Moreover, the hydrogen pickup characteristics of these alloys are improved over Zircaloy-2. For 750°F steam, the materials Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe are superior to Zircaloy-2 on the basis of corrosion resistance and strength; hydrogen-pickup properties are about the same as Zircaloy-2.

The data obtained for promising alloys in 680°F water were used for planning new ternary compositions. These materials are presently being evaluated for corrosion properties; since alloying addition concentrations were varied over rather specific limits, certain compositions should result in an optimum combination of corrosion, strength, and hydrogen-pickup properties. A similar procedure was employed for preparation of new ternary materials for 750°F steam corrosion resistance. At present, these alloys are being fabricated to sheet and autoclave test coupons. Although no satisfactory compositions were produced for corrosion resistance to 900°F steam, a number of alloys were markedly better than Zircaloy-2. This corrosion behavior suggested that further improvement was possible, and a comparatively small additional group of ternary alloys for this atmosphere has been planned.

III. PRINCIPAL INVESTIGATORS

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IV. STATEMENT OF PROBLEM

The program objective is the development of zirconium-base alloys having corrosion resistance, strength, and hydrogen-uptake characteristics superior to Zircaloy-2 in 680°F water and in 750° to 900°F steam.

V. DESCRIPTION OF WORK--RESULTS

The corrosion behavior of new ternary alloys in 680°F water is presented in Table I. Although the exposure time of 125 days is insufficient to allow for accurate evaluation of corrosion resistance, it is possible to make a cursory comparison with corrosion properties of the materials studied last year.

The first group of compositions shown in Table I was based on the alloy Zr-0.5Sn-0.25Te which, after 125 days' exposure to 680°F water, had a weight gain of 30.30 mg/dm^2. The modifications of alloying element concentration did not, apparently, improve the pretransition corrosion rate; it would seem that the original concentrations of tin and tellurium (or the Zr-0.5Sn-0.3Te alloy) result in the best corrosion resistance for this system when in the as-rolled condition. However, the time-to-transition and the post-transition corrosion rate--which are more important than the initial corrosion rate--have not yet been determined, and final evaluation of corrosion properties must be based on these parameters. For the alloy systems in Table I based on the compositions Zr-0.5Sn-0.25Ge and Zr-0.5Nb-0.25Te, a similar comparison may be drawn. However, alloys in the systems Zr-Sb-Nb and Zr-Cr-Te are markedly better than Zr-1Sb-0.5Nb and Zr-1Cr-0.25Te, respectively. The compositions Zr-Sb-Ge and Zr-Sb-Te are not as good as the base materials Zr-1Sb-0.25(Ge, Te). One should note, however, that most of the alloys in Table I exhibit corrosion properties equivalent or superior to Zircaloy-2, but a final comparison must take into account the hydrogen-pickup properties and tensile strength as well as time-to-transition and post-transition corrosion rate.

The group of alloys for 750°F steam application (Quarterly Report ARF-2198-31), which were based on results of ternary alloy studies last year, have been arc-melted and are presently being fabricated to sheet for corrosion evaluation. Based on data obtained for ternary compositions in 900°F steam, the materials planned for study in this atmosphere during the current year are presented in Table II. As yet these alloys have not been prepared. Although no materials previously studied were acceptable in 900°F steam, certain compositions were markedly superior to others; the alloys in Table II were based on these particular compositions.

VI. FUTURE WORK

Exposure of materials to 680°F water will be continued until the time-to-transition and the post-transition corrosion rate are reasonably well defined. Alloys for 750° and 900°F steam will be prepared for corrosion evaluation, and exposure to these atmospheres in autoclaves will begin. A 100-pound shipment of zirconium sponge has been received, and ingots (10 pounds) of promising alloys for 680°F water and 750°F steam service will be prepared by consumable arc-melting. The compositions to be prepared include the following:

Zr-0.5Nb-0.25Te
Zr-0.5Sn-0.25Ge

Zr-1Cr-0.25Te
Zr-1Sb-0.25Te
Zr-1V-1Fe
Zr-3Cr-1Fe
Zr-3Cr-0.25Te
Zr-0.5Nb-0.25Te

For these alloys, a detailed property evaluation will be carried out which will involve study of fabricability and weldability, determination of tensile and impact properties, and investigation of heat treatment effects on corrosion resistance. Current studies in 680°F water may indicate modification of the first four compositions above.

VII. CONCLUSIONS

A number of ternary compositions 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. These are compositions based on Zr-1Sb, Zr-1Cr, Zr-0.5Nb, and Zr-0.5Sn with minor additions of Te, Ge, Cr, or Fe. In 750°F steam, the materials Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe are initially acceptable on the basis of corrosion resistance and strength; however, hydrogen pickup is excessive. The current work is for the study of ternary alloys which are intended to show an optimum combination of corrosion, strength, and hydrogen-pickup properties. In addition, detailed evaluation of already promising compositions will be carried out.

VIII. REPORTS ISSUED

D. Weinstein and F. C. Holtz, "Development of Improved Zirconium Alloys for Use in Superheated Water and Steam," to be published in Proceedings, Symposium on Zirconium-Alloy Development, Vallecitos Atomic Laboratory, November 12, 1962.

Respectfully submitted,

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TABLE I

CORROSION PROPERTIES OF NEW TERNARY ALLOYS IN 680°F WATER

Composition, wt%	Weight Gain, mg/dm^2 14 days	42 days	84 days	125 days
Zircaloy-2	16.53	22.94	28.01	45.93
Zr-0.4Sn-0.4Te	14.34	18.56	26.15	30.37
Zr-0.5Sn-0.5Te	15.46	22.79	30.11	35.00
Zr-0.5Sn-0.3Te	12.94	18.60	24.26	29.11
Zr-0.5Sn-0.4Te	15.75	22.38	31.50	48.08
Zr-0.6Sn-0.3Te	13.95	20.93	26.35	32.55
Zr-0.75Sn-0.25Te	15.71	21.82	27.05	35.75
Zr-0.75Sn-0.4Te	14.56	21.45	27.58	34.48
Zr-0.9Sn-0.35Te	13.96	19.70	25.45	35.30
Zr-0.5Sn-0.3Ge	14.19	20.49	25.22	31.53
Zr-0.5Sn-0.4Ge	14.02	20.25	26.48	35.05
Zr0.75Sn-0.25Ge	14.62	23.08	30.01	41.55
Zr-0.75Sn-0.4Ge	15.07	21.86	27.13	33.16
Zr-0.9Sn-0.35Ge	15.56	22.24	27.42	38.54
Zr-0.75Sb-0.25Ge	17.32	28.34	37.00	41.73
Zr-0.75Sb-0.4Ge	18.73	28.50	37.45	44.78
Zr-1Sb-0.2Ge	19.93	29.06	37.37	53.15
Zr-1Sb-0.4Ge	19.65	30.29	35.20	48.30
Zr-1.2Sb-0.25Ge	19.78	30.06	37.18	52.21
Zr-1.2Sb-0.4Ge	20.66	32.22	50.40	--
Zr-1.5Sb-0.2Ge	20.41	31.06	39.93	56.79

TABLE I (continued)

Composition, wt%	Weight Gain, mg/dm^2 14 days	42 days	84 days	125 days
Zr-0.3Nb-0.5Te	14.84	22.69	32.30	40.15
Zr-0.4Nb-0.25Te	14.08	23.18	30.64	37.26
Zr-0.4Nb-0.4Te	43.19(crack)	--	--	--
Zr-0.5Nb-0.3Te	16.91	25.77	35.44	43.49
Zr-0.5Nb-0.4Te	15.62	21.87	30.46	36.71
Zr-0.75Nb-0.25Te	18.63	31.05	43.47	54.34
Zr-0.75Nb-0.4Te	18.47	31.55	43.86	53.87
Zr-0.75Sb-0.2Te	16.97	23.91	30.85	47.82
Zr-0.75Sb-0.3Te	18.41	26.21	35.41	53.83
Zr-0.75Sb-0.4Te	18.53	27.39	37.06	43.50
Zr-1Sb-0.2Te	15.55	23.32	30.32	38.87
Zr-1Sb-0.4Te	18.12	29.65	39.53	47.77
Zr-1.2Sb-0.15Te	24.29	35.56	--	--
Zr-0.75Sb-0.4Nb	14.97	21.27	27.57	32.30
Zr-0.75Sb-0.5Nb	15.52	22.18	28.09	34.01
Zr-1Sb-0.35Nb	16.23	23.97	30.15	50.25
Zr-0.75Cr-0.4Te	13.35	19.19	23.37	26.71
Zr-0.75Cr-0.5Te	13.27	19.91	25.71	29.03
Zr-0.85Cr-0.25Te	12.92	19.00	24.32	27.36

TABLE II

ALLOYS PLANNED FOR STUDY IN 900°F STEAM

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

TABLE II (continued)

Zr-1Mo-0.25Te
Zr-1Mo-0.25Sb
Zr-1Mo-1Fe
Zr-4Fe
Zr-5Fe