ARMOUR RESEARCH FOUNDATION
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IMPROVED ZIRCONIUM ALLOYS

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Quarterly Report
October 1, 1960 - December 31, 1960

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

February 2, 1961

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1. SUMMARY OF PROGRESS TO DATE

Approximately 100 binary zirconium alloys have been prepared for corrosion study leading to the development of improved zirconium alloys for service in superheated water and steam. Compositions were arc-melted, fabricated by hot rolling, and processed into small coupons for corrosion testing. Specifically, the binary compositions* under investigation are the following:

0.25, 1, 3, (each)	Fe, Co, Ni, Cu, Cr W, Mo, Ta, Te, Si Ge, As, Bi, Pb, Pt Pd, Rh, Ag, Au, In, Y
(0.5, 2, 5, 10, 20, 25, 30, 50, 75) Nb	
(0.5, 1.5, 3, 5, 7, 10, 12, 20) Sn	
(0.25, 1, 3, 5, 9) V	
(0.25, 1, 2.5, 4, 6, 10) Sb	

Based on an investigation of the zirconium-niobium system reported at the 1958 Geneva Conference, the following ternary alloys were prepared for initial study:

Zr-25Nb-1 (Sn, Sb, Cr, V, Fe, Cu, Pd)

Initial screening of experimental alloys in 680° F water for 168 hours has been completed. Compositions exhibiting corrosion resistance superior or comparable to Zircaloy-2 were further tested for an additional 187 hours; following this second evaluation, approximately 40 specimens still showed promise as possible bases for ternary and higher order alloys. These compositions have been placed back in test and will be exposed for five to six weeks. In addition, approximately 50 specimens showing promising corrosion behavior in 680° F water are being tested in 750° F steam.

* All compositions given in weight per cent.

II. PRINCIPAL INVESTIGATORS

D. Weinstein	-	Project Engineer
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III. STATEMENT OF PROBLEM

The program objective is development of alloys having superior 680°F water and/or 750° to 900°F steam corrosion resistance. Development of higher strength alloys for current temperature ranges while maintaining corrosion resistance comparable to that of Zircaloy-2 is also a major objective of this program. The effect of heat treatment on corrosion resistance will also be studied. Initially, corrosion behavior will be determined for a zirconium-niobium alloy in the fully retained-beta condition. The effect of zirconium purity on corrosion resistance and hydrogen pickup during corrosion will be determined on promising compositions.

IV. DESCRIPTION OF WORK--RESULTS

Since corrosion resistance is being used as the criterion for acceptance of experimental alloys, the major effort in this program has concentrated on corrosion testing. The results to date are presented in Table I, which lists those specimens exhibiting the desirable black, adherent oxide coating after the designated exposure times. In this relatively short-time corrosion test, specimen appearance is as important a criterion for acceptability as weight gain. After initial exposure in 680°F water for 168 hours, specimens not listed in Table I showed either excessively high weight gains, whitening of the oxide coating, or spalling and disintegration. After a 355-hour exposure, specimens marked with an asterisk were no longer considered to be promising in the alpha annealed condition and were not re-entered in corrosion testing. These compositions showed excessive weight gain and /or whitening of the oxide coating.

V. FUTURE WORK

At present, compositions listed in Table I which are not marked with an asterisk are being tested in 680°F water for an additional five to six weeks; corrosion behavior in 750°F steam is also being determined for these alloys. Since it has been observed that some compositions showing poor corrosion resistance in water have good corrosion

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TABLE I
CORROSION BEHAVIOR OF INITIALLY PROMISING
EXPERIMENTAL ALLOYS IN 680° F WATER

Composition	Weight Gain (mg/dm ²)	
	168 Hours	355 Hours
Zircaloy-2	15.17	21.00
Zr-0.5Nb	13.23	19.85
Zr-2Nb	23.72	27.67
Zr-5Nb*	35.53	45.68
Zr-10Nb*	41.64	52.81
Zr-25Nb	101.84	90.75
Zr-30Nb	39.75	55.04
Zr-0.5Sn	9.26	10.29
Zr-1.5Sn	13.32	18.44
Zr-3Sn	17.50	18.53
Zr-5Sn	13.26	16.32
Zr-7Sn	16.24	21.31
Zr-0.25V	21.35	23.38
Zr-1V	25.37	28.42
Zr-0.25Sb	12.02	26.44
Zr-1Sb	19.01	20.07
Zr-2.5Sb	20.93	25.12
Zr-4Sb	18.57	23.46
Zr-6Sb*	36.29	65.52
Zr-0.25Cr	11.33	12.36
Zr-1Cr	12.20	15.25
Zr-3Cr	23.93	29.91

TABLE I (continued)

Composition	Weight Gain (mg/dm ²)	
	168 Hours	355 Hours
Zr-0.25Cu	20.87	24.17
Zr-0.25Fe	9.17	10.19
Zr-1Fe	17.38	19.43
Zr-3Fe*	34.36	40.42
Zr-0.25Si	14.17	18.22
Zr-0.25W	7.17	11.27
Zr-1W	13.20	39.59
Zr-0.25Mo	10.12	14.17
Zr-1Mo	14.10	21.15
Zr-0.25Ta	10.93	12.92
Zr-0.25Co	18.38	21.62
Zr-1Co	17.91	22.04
Zr-3Co	19.75	22.87
Zr-0.25Bi*	13.34	40.03
Zr-0.25Pt	17.40	19.57
Zr-1Pt	22.79	28.22
Zr-0.25Pd	24.72	29.02
Zr-1Pd	24.99	30.25
Zr-0.25Rh	20.94	24.87
Zr-1Rh	11.88	15.84
Zr-1Ag	20.68	22.86
Zr-.25As	9.84	13.12
Zr-1As	19.14	21.87
Zr-0.25Te	13.15	17.53
Zr-1Te	25.03	30.47
Zr-0.25Ge	17.21	21.18
Zr-1Ge*	28.32	37.04

TABLE I (continued)

Composition	Weight Gain (mg/dm ²)	
	168 Hours	355 Hours
Zr-0.25Ni	22.65	24.81
Zr-1Ni	23.82	27.07
Zr-3Ni*	47.07	55.44
Zr-25Nb-1Sn	37.60	46.67
Zr-25Nb-1Sb*	57.83	63.18
Zr-25Nb-1Cr*	58.47	76.88
Zr-25Nb-1V*	49.26	69.61
Zr-25Nb-1Pd*	55.82	66.77

* Specimen showed excessive weight gain and/or whitening of the oxide coating after 355 hours exposure--removed from further testing.

behavior in high-temperature steam, a number of alloys will be exposed to 900°F steam. The data obtained from these tests will be used for planning of ternary and higher order alloys.

Two topics of research are expected to commence in the near future. These are the effect of zirconium purity and the effect of heat treatment on corrosion resistance. In previous ARF studies conducted on electron-beam melted zirconium, one specimen did not exhibit the characteristic "pepper-like" precipitate in the microstructure. This specimen had corrosion resistance superior to identically processed material which contained the precipitate. No marked impurity differences were detected. Thus, five specimens (four of iodide zirconium, one of sponge) have been shipped to Alloy Research Corporation, Cambridge, Massachusetts, for electron-beam melting. Metallographic examination and corrosion testing will be carried out on this material.

For investigation of the effect of heat treatment on corrosion resistance, a series of zirconium-niobium alloys were beta-quenched from 1000°C. The Zr-30Nb alloy, which so far exhibits fair corrosion behavior, had a clean, retained beta microstructure and would seem ideally suited for this study. Prior work at Oak Ridge National Laboratory indicates that beta at 680°F can be stabilized by additions of molybdenum. Pertinent experiments related to this investigation are now being carried out.

Experiments on hydrogen pickup during corrosion will be carried out on only the most promising compositions. Mechanical property investigations may be similarly limited. Therefore, initiation of these studies must await the results of corrosion testing.

VI. CONCLUSION

A program has been outlined which approaches development of zirconium alloys by corrosion screening of binary alloys. The results obtained from these studies will be used for planning ternary and higher order alloys. The program is a search for a major improvement over Zircaloy; therefore, a wide range of binary alloys is being studied. Due to the large number of alloys under investigation as well as the wide work scope of this program, no definite experimental conclusions can be presented at

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this time. Experimental work is proceeding toward accomplishing the objective of developing alloys superior to currently available materials.

VII. REPORTS ISSUED

D. Weinstein, R. J. Van Thyne, and D. W. Levinson,
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Respectfully submitted,

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