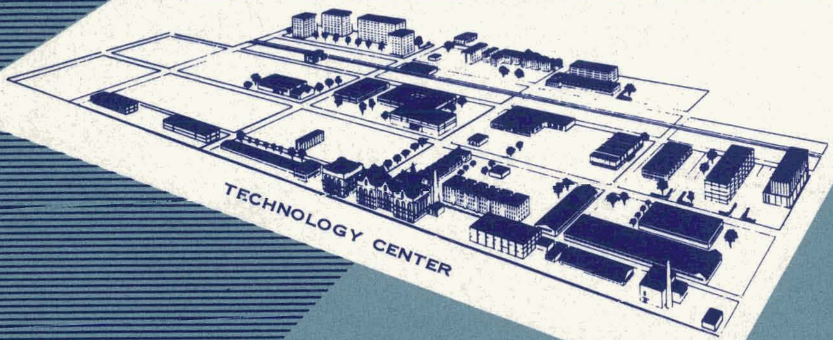
MASTER

ARF 2198-13
(Summary Report)
EURAEC-89

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY



IMPROVED ZIRCONIUM ALLOYS

EURATOM PROGRAM

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

U.S.A.E.C. Offices and Direct Contractors
engaged on the Relevant Project Only

LEGAL NOTICE

This document was prepared under the sponsorship of the United States Atomic Energy Commission pursuant to the Joint Research and Development Program established by the Agreement for Cooperation signed November 8, 1958 between the Government of the United States of America and the European Atomic Energy Community (Euratom). Neither the United States, the U. S. Atomic Energy Commission, the European Atomic Energy Community, the Euratom Commission, nor any person acting on behalf of either Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

As used in the above, "person acting on behalf of either Commission" includes any employee or contractor of either Commission or employee of such contractor to the extent that such employee or contractor or employee of such contractor prepares, handles, disseminates, or provides access to, any information pursuant to his employment or contract with either Commission or his employment with such contractor.

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

IMPROVED ZIRCONIUM ALLOYS

D. Weinstein
F. C. Holtz
R. J. Van Thyne

Summary Report
April 1, 1960 - January 31, 1961

Contract No. AT(11-1)-578
Project Agreement No. 1
(EURAEC-89)

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

February 28, 1961

IMPROVED ZIRCONIUM ALLOYS

ABSTRACT

The objectives of this program are the development of zirconium-base alloys possessing exceptionally good corrosion resistance to 680° F water or 750° -900° F steam and/or improved strength at elevated temperatures. Approximately 100 binary compositions were prepared and screened by corrosion testing in 680° F water; selected compositions were exposed to 750° F steam. The data obtained indicate promising bases for ternary and quaternary alloys. Related investigations involving zirconium purity and heat treatment for improvement of corrosion properties are proceeding. Hydrogen pickup and mechanical properties will be used as acceptability tests on promising compositions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

IMPROVED ZIRCONIUM ALLOYS

I. INTRODUCTION

This report summarizes work performed during the period April 1, 1960 to January 31, 1961, on Contract No. AT(11-1)-578, Project Agreement No. 1, "Improved Zirconium Alloys."

At the present operating temperature of pressurized water reactors (approximately 600°F), Zircaloy-2 meets most of the requirements for a fuel cladding material. However, higher reactor temperatures would result in more efficient designs and provide cheaper nuclear power. At temperatures not much above 600°F, Zircaloy-2 has inadequate corrosion resistance and lacks desired strength as a fuel cladding. With the need for improved zirconium alloys apparent, this program has the objective of developing alloys markedly superior to those currently available. Specifically, the alloys to be developed should possess exceptionally good corrosion resistance to 680°F water or 750°-900°F steam and/or should exhibit improved strength at elevated temperatures.

During the past decade, considerable research and development efforts were carried out on zirconium. However, the relatively immediate success of Zircaloy seemed to have retarded progress in further zirconium alloy development. This observation is exemplified by the voluminous accumulation of data available on minor compositional variations of Zircaloy. In more recent years, comparatively higher concentrations of alloying elements were employed in development programs. Very few of these programs systematically investigated binary alloys which might then be used for development of ternary, quaternary, and higher order compositions. As a result, corrosion data on binary compositions--other than for relatively dilute alloys--remain incomplete. Although some very promising compositions have resulted from past work, no significant improvements over Zircaloy were achieved for higher temperature operation.

In the present program, a comparatively large-scale, binary alloy corrosion screening investigation has been carried out. Ultimately, the data obtained on binary compositions should provide ternary bases and indicate the elements having a beneficial effect on corrosion resistance. By this procedure, it is hoped that a major improvement over Zircaloy will result.

At the beginning of this program, an Interim Report(1) was prepared summarizing current work on development of improved zirconium alloys. Information was obtained by contact with investigators in this field and used for planning the binary alloy corrosion screening program. In addition, a good picture of the present state of zirconium alloy development was obtained. In superheated water, for example, preliminary data indicate that some alloys possess corrosion resistance and/or strength superior to Zircaloy-2. Hydrogen pickup during corrosion seems to be the factor limiting acceptability; the phenomenon and all its ramifications are not fully understood. In superheated steam, expecially at 900-1000° F, no alloy seems to possess the required corrosion resistance, strength, and minimum hydrogen pickup.

II. SCOPE OF INVESTIGATION

During the initial planning stage of this program, several areas of research were conceived--namely, binary alloys, ternary and higher order alloys, effects of heat treatment on corrosion resistance, mechanical property determination, zirconium purity effects, and pickup of corrosion hydrogen.

At this writing, two more months of experimental work remain. Of the six areas outlined above, studies are proceeding in all but the last phase of the program. Data on binary alloys in superheated water and steam have been obtained, and a limited ternary alloy investigation has been carried out. Initial experiments on zirconium purity and heat treatment effects have been initiated; however, final determination of these effects by evaluation of corrosion properties has not yet started. A number of specimens are being prepared for mechanical property tests, and data will be available by the end of the current contract period. Determinations of hydrogen pickup during corrosion have not been initiated.

A. Binary Alloys

For investigation of the corrosion behavior of binary alloys in superheated water and steam, the following compositions were chosen:

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

In addition, more intensive study was planned on elements known to improve corrosion resistance in water or steam when present as relatively small additions. For this investigation, the following alloys were prepared:

(0.5, 2, 5, 10, 20, 25, 30, 50, 75)Nb
(0.5, 1.5, 3, 5, 7, 10, 20)Sn
(0.25, 1, 3, 5, 9)V
(0.25, 1, 2.5, 4, 6, 10)Sb

Considerable effort was devoted toward avoiding duplication of work done by other organizations;(1) however, a number of alloying additions previously shown to be beneficial were employed. A number of additives were chosen by their relationship within the periodic table to beneficial elements. In addition, some compositions were chosen because of incomplete investigation, and others were selected for the fundamental knowledge of their effect on corrosion behavior.

B. Ternary and Higher Order Alloys

Basically, the choice of ternary alloys should be guided by corrosion data on binary alloys. In this way, the most logical and direct approach to successful alloys can proceed. However, an investigation(2) of the zirconium-niobium system indicated that a corrosion minimum might exist at the composition Zr-25Nb. Because of this possible attractive corrosion behavior as well as the possibility of retaining the beta phase, the following ternary alloys were prepared for initial study:

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

---

* All compositions are given in weight per cent.

C. Heat Treatment and Microstructure

The effect of heat treatment on corrosion resistance has not received adequate attention. It is not known, for example, how a metastable retained-beta alloy compares with an alloy of the same composition having a microstructure of equilibrium transformation products. Thus, for certain heat treatable systems such as Zr-Nb, compositions having various microstructures were to be corrosion tested. Other compositions showing good corrosion resistance in the equilibrium condition would be considered for heat treatment studies.

D. Zirconium Purity

In some exploratory ARF work by Levinson(3) on electron-beam refining, a specimen of iodide zirconium was produced which did not exhibit the characteristic "pepper-like" precipitate. The corrosion resistance of this refined material was superior to identically processed iodide zirconium which did show the precipitate and had a higher hardness. No explanation was given for the difference in corrosion behavior or microstructural appearance, nor was mention made of any change in composition. On the basis of this work, investigation of zirconium purity effects on corrosion resistance was conceived. Promising alloys would be prepared from exceedingly high-purity iodide zirconium.

E. Hydrogen Pickup During Corrosion

In recent years, the problem of hydrogen pickup during corrosion and subsequent concentration by thermal gradients has received considerable attention.(4, 5) The possible embrittlement accompanying hydrogen pickup could be the eliminating factor in acceptability of an alloy. The investigation of hydrogen pickup provides a thorough analysis of the factors involved in corrosion. Therefore this factor will be evaluated on alloys exhibiting promising corrosion behavior.

F. Mechanical Properties

Strength, ductility, impact resistance, and other mechanical properties are of prime importance in considering an alloy for use as cladding material. For alloys showing good corrosion resistance, strength at elevated temperature would be determined.

III. MATERIALS, APPARATUS, AND EXPERIMENTAL PROCEDURES

A. Materials

The quality and description of some of the materials used in preparation of alloys is summarized below, and all available information obtained from the supplier is presented. Most of the alloying elements used in this program were available from Foundation melting stock; in all cases the purity was at least 99 per cent. In some cases purity was as high as 99.999+ per cent.

Zirconium: High-quality sponge (75 pounds) was obtained from Wah Chang Corporation, Albany, Oregon. Arc-melted hardness = 105 VHN. (For chemical analysis see Table I). Iodide zirconium, obtained from Westinghouse is presently being electron-beam refined for use in studying the effect of zirconium purity on corrosion resistance.

Niobium: Electron-beam-melted niobium in the form of 0.060 inch thick sheet (3.9 pounds) was obtained from Wah Chang Corporation. As-cast hardness = 74 BHN. (For chemical analysis see Table I.)

Tin: The Vulcan Detinning Company, Sewaren, New Jersey, supplied 10 pounds of "extra pure" tin, 99.998+ per cent. The major impurities were:

Pb < 0.001 w/o
Fe < 0.00005 w/o
total foreign metal < 0.002 w/o

Antimony: Reagent grade antimony chips, 99.8 per cent pure, were used in preparation of alloys.

Vanadium: Produced by the calcium-reduction process, the vanadium is 99.8 per cent pure with carbon and oxygen being the major contaminants.

For standardization and calibration of autoclaves, 2.6 pounds of cold-rolled (0.030 inch thick) Zircaloy-2 was obtained from Bettis Atomic Power Laboratory, Pittsburgh, Pennsylvania. The strip was prepared from ingot No. D-141 for which the corrosion behavior is 680° F water and 750° F

TABLE I

SUPPLIER'S IMPURITY ANALYSIS OF SPONGE ZIRCONIUM AND ELECTRON-BEAM-MELTED NIOBIUM

Impurity	Impurity Content, ppm	
	Zr	Nb
Al	32	< 20
B	< 0.2	< 1
C	---	< 30
Cd	< 0.3	< 5
Co	< 5	---
Cr	30	< 20
Cu	< 20	< 20
Fe	150	< 100
Hf	55	< 80
Mg	170	< 20
Mn	15	< 20
Mo	10	20
N	20	57
Ni	< 10	< 20
O	670	185
Pb	5	< 20
Si	30	< 100
Sn	< 5	< 20
Ta	---	445
Ti	< 20	< 150
V	< 20	< 20
W	< 40	105
Zn	---	< 20
Zr	---	< 500

steam and has been determined for exposure times up to 280 days. The four-pound quantity of iodide zirconium (crystal bar), also obtained from Westinghouse, has an arc-melted hardness of 76 VHN. No chemical analysis is presently available, but the lower hardness indicates a higher purity level than that of the sponge melting stock.

B. Fabrication

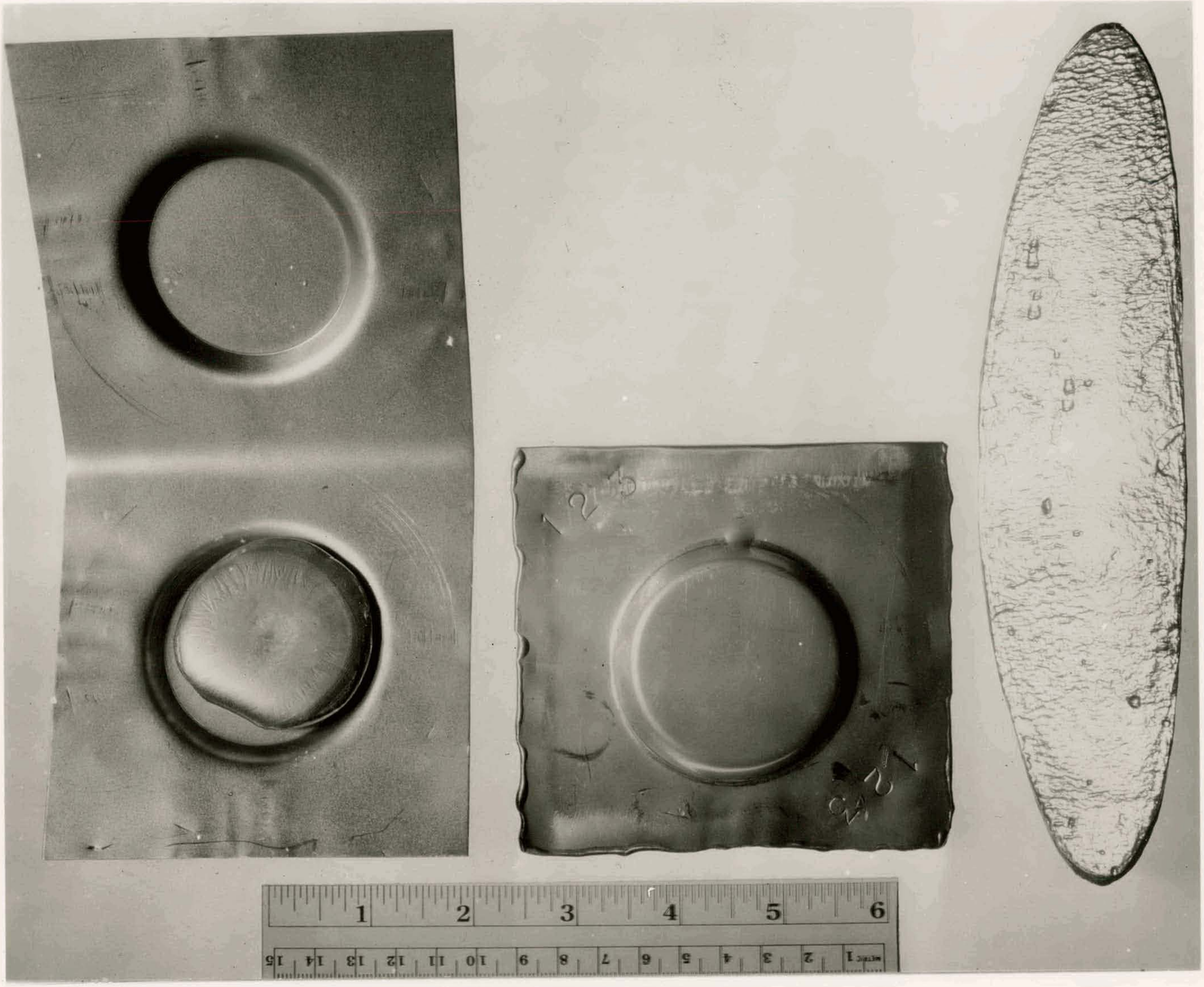
Alloys of 100 grams were prepared by accurately weighing components on an analytical balance followed by nonconsumable arc melting. An 800-amp welding generator powers the arc-melting furnace which employs a water-cooled tungsten electrode and a water-cooled copper hearth. An argon atmosphere (positive pressure) is provided by evacuating and backfilling twice before melting. To insure homogeneity, all specimens were turned over and remelted five times. Alloys containing tungsten, molybdenum, or tantalum were prepared by first making a Zr-50X master alloy.

The furnace atmosphere was tested by remelting small ingots of titanium; the uniform hardness of these control melts assured the absence of contamination. Loss of constituents by volatilization, or contamination by electrode or crucible material was checked by weighing the ingots after melting.

Following the melting operation, the ingots were sealed in a low-carbon, "killed" steel jacket to avoid contamination by air during subsequent fabrication. A photograph of this procedure is shown in Figure 1. The "can" is sealed by heliarc-welding the edges.

The procedure used in rolling ingots attempts to produce sheet essentially free of edge cracking and atmospheric contamination. Furthermore, attaining a constant or similar microstructure for all compositions shoud render corrosion data and comparisons more meaningful. With these fabrication objectives in mind, the following rolling and annealing procedure was devised:

1. Anneal 15 canned ingots approximately 0.45 inch thick at 1550°F for 1 hour.
2. Roll to 0.295 inch thick at 1550°F, using a 10 per cent reduction per pass.



Neg. No. 20385

Figure 1

Canning procedure for prevention of air contamination during fabrication. Rolled ingot is shown at right.

3. Anneal at 1550°F for 1 hour.
4. Roll to 0.157 inch thick at 1550°F using a 10 per cent reduction per pass. Total time at 1550°F is about 4 hours.
5. Anneal and work below transformation temperatures. For all alloys except Zr-Nb, anneal 1 hour at 1350°F, roll at this temperature to 0.110 thick, using 10 per cent reduction per pass. Anneal 1 hour at 1350°F, and air cool. For Zr-Nb alloys, use 1090°F instead of 1350°F.

Since corrosion resistance is used as the initial criterion of acceptance, corrosion coupons (approximately 5/8 x 1 x 0.043 inch) are prepared from as-rolled sheet. The steel jacket is stripped off (Figure 1), and slightly oversize corrosion specimens are cut from the center of the sheets. (The material remaining can be used for another corrosion specimen, a tensile specimen, and metallographic specimens.) The surfaces and edges are milled to remove any iron contamination (thickness of specimen is approximately 0.050 inch), and lapping provides extremely smooth surfaces. Edges are hand polished on No. 000 emery paper. Coupons are then degreased in petroleum ether and ethyl alcohol, and a hole is drilled for suspending the coupon on the stainless steel test rack.

C. Corrosion Testing

The techniques employed in preparing specimens for autoclave testing as well as actual testing procedures have closely followed specifications outlined by Kass.(6, 7) The cleaned and identified coupons are rinsed in hot tap water and etched in a solution of $5HF-45HNO_3-50H_2O$ at 90-100°F. Rinsing follows in a series of flowing tap water—high purity water baths, and drying is accomplished by immersing in ethyl alcohol followed by a warm air blast. A cursory check of thickness is made to insure removal of at least 0.006 inch of metal. This technique produces a bright, metallographic type surface free of stains or imperfections. Specimens are stored in clean, capped bottles, and immediately prior to corrosion testing, coupons are very accurately measured and weighed.

Before the first autoclave test, standardized procedure(6, 7) was followed in cleaning parts. The cleaning involved passivation of the test rack and numerous detergent scrubbings and water rinses of the inner chamber. The autoclave was checked by exposing five specimens of Ziraloy-2 to 680° F water for seven days. Standardized procedure was used in filling and stabilizing the autoclave; temperature was controlled within ± 2°F, and the test water was double distilled-demineralized having a pH of 7 and a resistivity in the range of 1-2 million ohm-centimeters. The weight gains of these five specimens were consistent with corrosion data supplied by Westinghouse on this particular heat of Zircaloy-2.

For testing in steam, a static atmosphere is maintained by means of two interconnected autoclaves as schematically shown in Figure 2. One autoclave acts as a steam generator and reservoir, and the other serves as the testing chamber. A 7-day trial run on five specimens of Zircaloy-2 was carried out at 750° F and 1500 psi pressure. The weight gains agreed with those previously determined at Bettis.

IV. RESULTS

A. Fabrication and Microstructure

The fabrication techniques used in producing sheet from the arc-melted ingots were generally satisfactory for all compositions. There were, nevertheless, a few notable exceptions, especially in alloys containing high solute concentrations. For example, compositions containing 20 to 50 per cent niobium exhibited edge cracking which increased in severity at the higher niobium concentrations. Binary alloys containing up to 12 per cent tin were rolled without difficulty; however, the 20 per cent tin composition "fishtailed" into two pieces. No difficulties were encountered with vanadium alloys, but Zr-10Sb was severely edge cracked. Similarily, the ternary compositions, Zr-3Fe, and Zr-3Si showed various degrees of edge cracking. After exposure to 680° F water for 168 hours the Zr-3Te alloy exhibited areas of severe attack which could have been due to fine cracks in the specimen. With the exception of Zr-20Sn, a corrosion specimen could be cut from each sheet.

The rolling procedure was, within limits of phase equilibria, successful in producing a "constant" microstructure for all specimens. Most of the equilibrium diagrams are the beta-eutectoid type having essentially

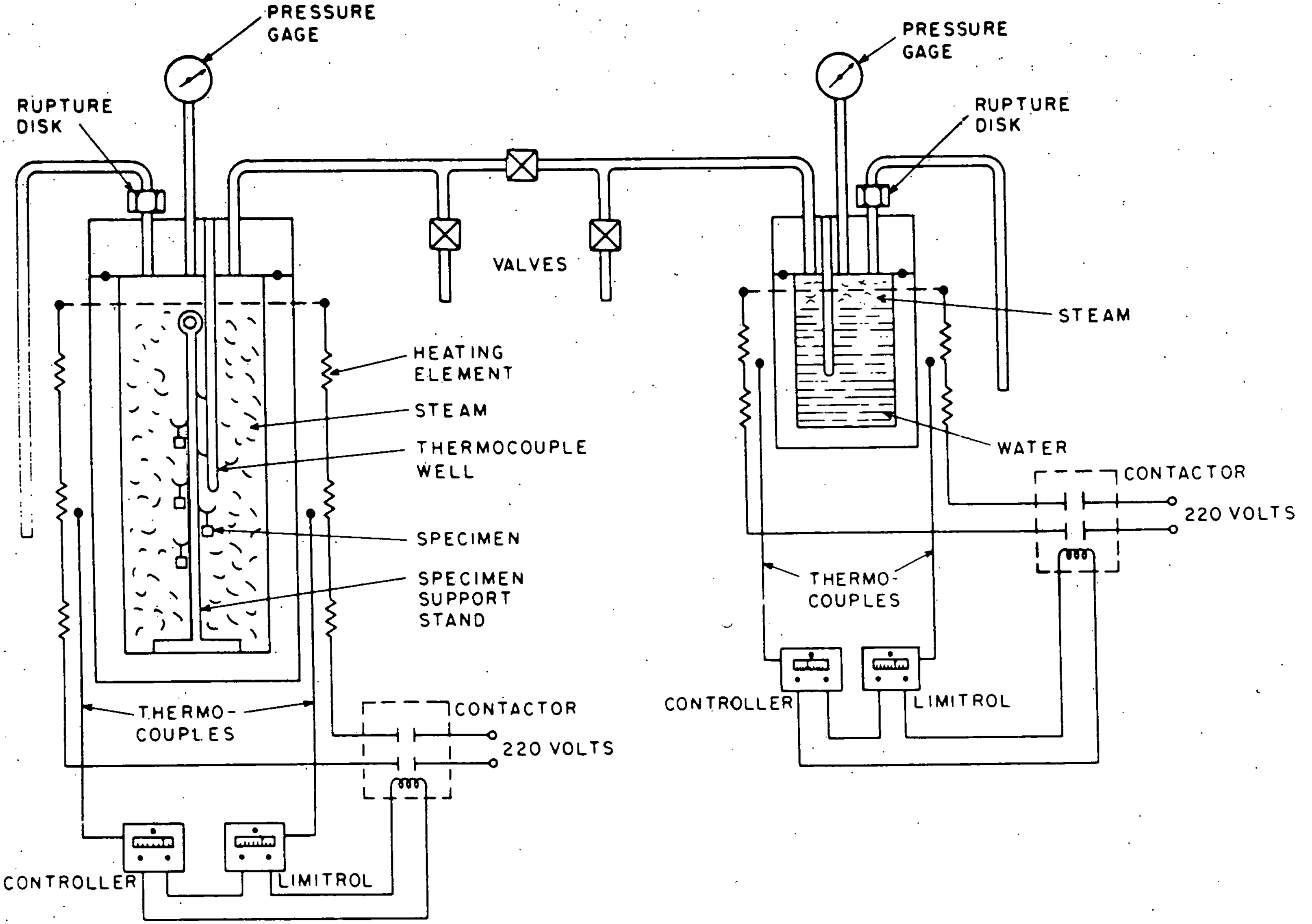


FIGURE 2 - SCHEMATIC DIAGRAM OF AUTOCLAVE SYSTEM FOR TESTING IN SUPERHEATED STEAM.

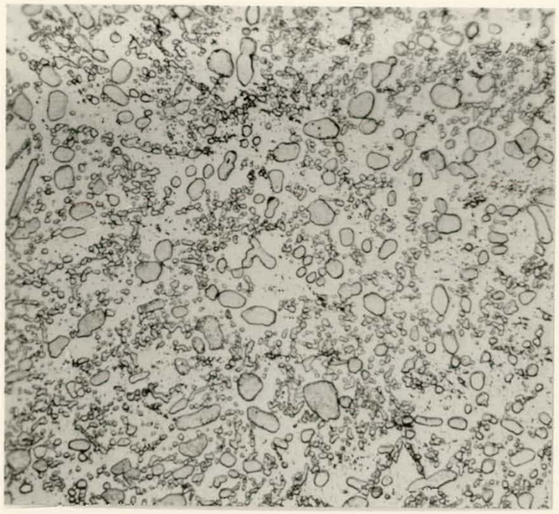
no solid solubility in zirconium and an intermetallic compound as the equilibrium phase with unalloyed zirconium. For these systems, Figures 3, 4, and 5 represent the typical as-rolled microstructure. While these structures initially look different, the type of phases present are identical. The occurrence of the intermediate phase and the alpha-zirconium account for the differences in appearance. For example, in Figure 3 (Zr-3Fe) the intermetallic compound $ZrFe_2$ occurs as globules in an alpha-zirconium matrix. In Zr-3Ag (Figure 4), alpha occurs as a coarse Widmanstatten structure with the intermediate phase ZrAg concentrated between alpha platelets. Figure 5 (Zr-3Mo) is essentially the same as Figure 4, except that the structure is much finer.

Figure 6 is representative of systems having alpha-stabilized type equilibrium diagrams where the alloy composition is within the solid solution alpha-zirconium with possibly a very small amount of Zr_4Sn precipitate due to air cooling from 1350° F. Of course, compositions beyond the limit of solid solubility would show greater amounts of intermetallic compound.

Work on the metallography and phase equilibrium of the zirconium-niobium system is noteworthy due to the large number of conflicting results obtained by other investigators. The original phase diagram for this system was determined by Rogers and Atkins,(8) who found the solubility limit of niobium in zirconium to be 6.5 weight per cent. Figure 7, however, shows a Zr-5Nb alloy which was rolled and annealed at 1090° F (588° C) and is clearly two-phase. Domagala and McPherson(9) first pointed out this discrepancy while working with a similar composition. More recently, Lundin and Cox(10) have redetermined the complete diagram and found the solubility limit to be 0.6 weight per cent. This diagram appears to be more reliable. In addition, there is disagreement on the eutectoid (monotectoid) temperature. Very recently Anderko(11) has determined this temperature to be 590° C. Others(8, 10) have reported the eutectoid at 610° C. No investigation of phase equilibria has been carried out in the present program.

B. Corrosion Behavior

Since corrosion resistance is being used as a criterion for acceptance of experimental alloys, the major effort in this program has



Neg. No. 20760 Mag. X500

Figure 3

Zr-3Fe, as-rolled. Globular particles of $ZrFe_2$ in an alpha zirconium matrix.

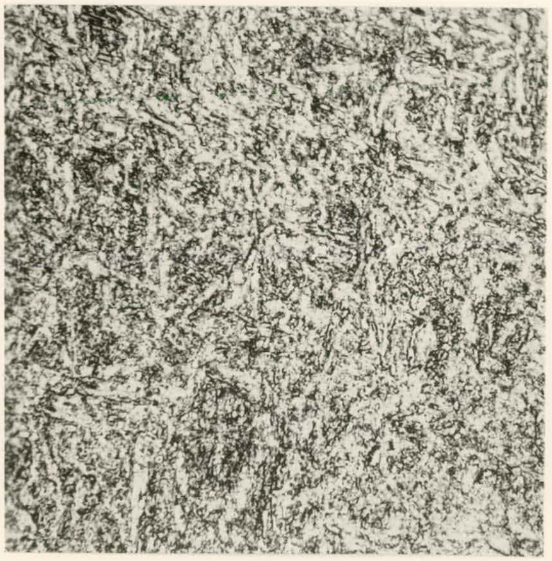
Etchant: 1 HF, 1 HNO_3, 3 glycerin

Neg. No. 20761 Mag. X500

Figure 4

Zr-3Ag, as-rolled. Fine particles of ZrAg between Widmanstatten alpha-zirconium.

Etchant: 1 HF, 1 HNO_3, 3 glycerin

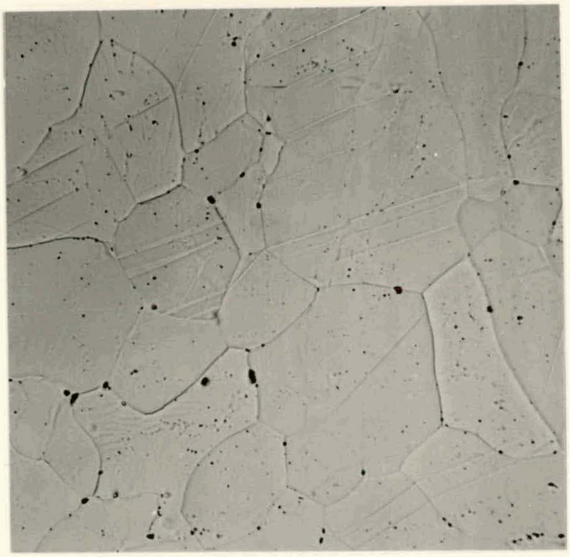


Neg. No. 20762 Mag. X500

Figure 5

Zr-3Mo, as-rolled. Extremely fine Widmanstatten alpha-zirconium platelets with partially decomposed beta and $ZrMo_2$.

Etchant: 1 HF, 1 HNO_3, 3 glycerin



Neg. No. 20763 Mag. X500

Figure 6
Zr-3Sn, as-rolled. Alpha-zirconium solid solution with possibly a small amount of Zr_4Sn precipitate at grain boundaries.

Etchant: 1 HF, 1 HNO_3, 3 glycerin.

Neg. No. 20764 Mag. X250

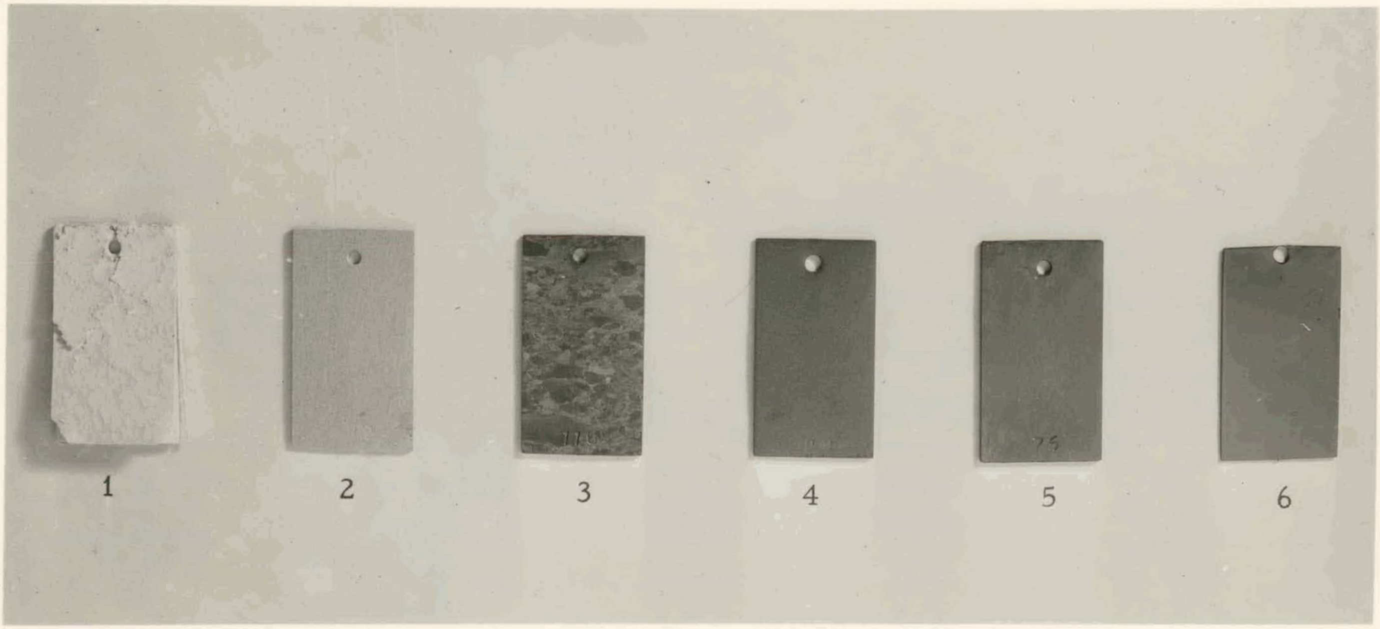
Figure 7
Zr-5Nb, as-rolled (annealed at 588° C). Two-phase structure showing grain boundary and Widmanstatten alpha and equilibrium, niobium rich beta-prime or possibly partially decomposed beta.

Etchant: 1 HF, 1 HNO_3, 3 glycerin.

concentrated on corrosion testing. To date, all compositions originally planned--with the exception of indium and yttrium alloys--have been corrosion tested in 680°F water for 168 hours. These conditions were used for initial screening of materials.

From the standpoint of corrosion resistance, zirconium alloys are evaluated by weight gain and appearance of the oxide coating. (Hydrogen pickup during corrosion has been used in other investigations as a screening test; however, in this program it will be used in final evaluation of promising compositions.) In general, corrosion specimens having a low weight gain will also have the desirable black, lustrous, adherent oxide coating. In a relatively short time test, however, the formation of a white oxide coating will indicate a poor specimen regardless of the initial weight gain. The appearance of the oxide coatings formed on zirconium alloys during water corrosion is represented in Figure 8. Specimens 1 and 2 represent extremely poor resistance to 680°F water having both high weight gains and heavy, white oxide coatings. Specimen 3 shows the first signs of formation of the white oxide coating, and specimen 4 has a gray, tenacious coating and a high weight gain. Possibly with the exception of specimen 4, the appearance of the oxide alone would be sufficient evidence for rejection of these compositions. Specimen 5 has a lustrous, heavy, black oxide coating (not brought out well in photograph) and is rejected simply for the high weight gain. Specimen 6 represents the desired specimen appearance--a lustrous, thin, black, tenacious coating.

Table II presents weight gain data on alloys considered to be promising. Initially, all compositions were exposed to 680°F water for 168 hours; rather than list every weight gain, only the data for alloys initially considered acceptable are presented. The remaining compositions, after 168 hours, showed either extremely high weight gains, whitening of the oxide coating, and/or spalling and disintegration. These specimens were eliminated from further testing, and the alloys listed were further exposed to 355 hours. At this point, compositions marked with an asterisk in Table II showed relatively high weight gains and whitening of the oxide coating. They were no longer considered promising alloys in the as-rolled condition, and were not further tested.



Neg. No. 20727 Actual Size

Figure 8

Oxide appearance on zirconium alloy corrosion specimens (680°F water).

1. Zr-3Ta: heavy, white, spalling coating--extremely poor corrosion resistance.
2. Zr-3Ge: white, adherent coating--very poor corrosion resistance.
3. Zr-5Nb: limited stage of white oxide formation--poor corrosion resistance.
4. Zr-3Ni: gray, adherent coating--high weight gain, poor corrosion resistance.
5. Zr-3Bi: heavy, black, lustrous, coating--high weight gain, poor corrosion resistance.
6. Zircaloy: thin, black, lustrous, adherent coating--low weight gain, good corrosion resistance.

TABLE II

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

	Weight Gain (mg/dm^2)	
Composition	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 II (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-0.25As	9.84	13.12
Zr-1As	19.14	21.87
Zr-0.25Te	13.15	17.53
Zr-1Te	25.03	30.47

TABLE II (continued)

Composition	Weight Gain (mg/dm^2) 168 Hours	Weight Gain (mg/dm^2) 355 Hours
Zr-0.25Ge	17.21	21.18
Zr-1Ge*	28.32	37.04
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

* After 355 hours, compositions no longer appeared promising in as-rolled condition and were removed from test.

The remaining compositions of Table II were returned to 680° F water for additional testing. Table III presents the results after a total exposure of 1043 hours. Once again, at this juncture a number of compositions were judged as having unacceptable corrosion resistance and would offer little hope of further development into successful alloys. These alloys are designated with an asterisk. The remaining compositions have been replaced in 680° F water for determination of long-time corrosion properties.

Based on preliminary results of corrosion behavior in 680° F water, a number of compositions were exposed to 750° F steam (pressure = 1500 psi) for 329 hours. The results of this test are summarized in Table IV. In general, corrosion in 750° F steam was much more severe than in 680° F water; however, there are exceptions. Interesting and possibly encouraging trends in corrosion behavior of the Zr-Sn and Zr-V systems are noted; further mention of data and comparisons of results will be made under Section V, DISCUSSION. Compositions in Table IV which are not designated with an asterisk have been replaced in 750° F steam for obtaining longer-time corrosion data. Since one objective of this program is development of improved alloys in high-temperature steam, a group of compositions are being tested in 900° F steam. Alloys which exhibited promising corrosion resistance to 750° F steam were among those selected for the higher-temperature tests. Although data are not yet available, the compositions presently being tested are summarized in Table V. It is anticipated that a few alloys which did not possess exceptional corrosion behavior at lower temperatures may exhibit superior corrosion resistance at 900° F.

C. Heat Treatment

The initial study of the effect of heat treatment on corrosion resistance will involve testing of an alloy in the retained beta condition. The zirconium-niobium system is presently being considered for this investigation; previous work has shown that, above certain niobium contents, beta can be retained at room temperature by quenching. Unfortunately, no beta-isomorphous systems are known to exist in zirconium binary alloys. Therefore, before corrosion testing can proceed, two behavior characteristics must be established: (a) the as-quenched specimen must be fully retained beta; (b) during exposure

TABLE III

RESULTS OF FURTHER EXPOSURE OF INITIALLY PROMISING ALLOYS IN 680°F WATER

Composition	1043-Hour Weight Gain (mg/dm^2)
Zircaloy-2	25.42
Zr-0.5Nb	27.57
Zr-2Nb	47.44
Zr-25Nb*	126.04
Zr-30Nb	98.86
Zr-0.5Sn	20.58
Zr-1.5Sn	28.68
Zr-3Sn	31.91
Zr-5Sn	26.52
Zr-7Sn*	61.90
Zr-0.25V	29.49
Zr-1V	38.58
Zr-0.25Sb*	335.64
Zr-1Sb	30.64
Zr-2.5Sb	37.68
Zr-4Sb*	53.77
Zr-0.25Cr	19.57
Zr-1Cr	23.38
Zr-3Cr*	67.82
Zr-0.25Cu	30.76
Zr-0.25Fe	22.42
Zr-1Fe	36.82

TABLE III (continued)

Composition	1043-Hour Weight Gain (mg/dm^2)
Zr-0.25Si	33.39
Zr-0.25W	14.34
Zr-1W*	256.82
Zr-0.25Mo	22.26
Zr-1Mo*	52.33
Zr-0.25Co	21.86
Zr-0.25Co	31.35
Zr-1Co	27.55
Zr-3Co	38.47
Zr-0.25Pt	28.27
Zr-1Pt	46.67
Zr-0.25Pd	44.06
Zr-1Pd	49.98
Zr-0.25Rh	36.65
Zr-1Rh	26.40
Zr-1Ag	33.73
Zr-0.25As	21.87
Zr-1As	16.40
Zr-0.25Te	24.12
Zr-1Te	47.88
Zr-0.25Ge	35.73
Zr-0.25Ni	34.52
Zr-1Ni	41.14
Zr-25Nb-1Sn	66.12

* After 1043 hours, specimen was removed from further testing.

TABLE IV

INITIAL CORROSION TEST IN 750° F STEAM

Composition	329-Hour Weight Gain (mg/dm^2)	Remarks
Zircaloy-2	24.88	
Zr-0.5Nb	27.42	
Zr-2Nb	51.20	
Zr-5Nb*	72.20	
Zr-10Nb	101.75	
Zr-25Nb*	136.46	
Zr-30Nb*	134.73	
Zr-0.5Sn*	Loss	Spalling, Disintegration
Zr-1.5Sn*	1202.88	Spalling, Disintegration
Zr-3Sn*	4763.23	Spalling
Zr-5Sn	603.63	
Zr-7Sn	252.18	
Zr-0.25V*	277.41	Spalling
Zr-1V	27.19	
Zr-3V*	Loss	Spalling, Disintegration
Zr-0.25Sb*	1745.0	Spalling
Zr-1Sb	29.51	
Zr-2.5Sb	37.01	
Zr-4Sb	41.65	
Zr-6Sb	75.40	
Zr-0.25Cr	22.44	
Zr-1Cr	58.44	
Zr-3Cr	23.09	
Zr-0.25Cu	24.78	
Zr-0.25Fe	26.77	

TABLE IV (continued)

Composition	329-Hour Weight Gain (mg/dm^2)	Remarks
Zr-1Fe	27.79	
Zr-3Fe	38.65	
Zr-0.25Si*	56.96	Spalling
Zr-0.25W*	671.19	Spalling, Disintegration
Zr-1W*	652.00	Spalling
Zr-0.25Mo	17.04	
Zr-1Mo	20.08	
Zr-0.25Ta	35.31	
Zr-0.25Bi*	1481.27	Spalling
Zr-0.25Co	38.90	
Zr-1Co	27.30	
Zr-3Co	33.13	
Zr-0.25Pt	37.84	
Zr-1Pt*	54.43	
Zr-0.25Pd	34.53	
Zr-1Pd	48.83	
Zr-0.25Rh*	40.31	
Zr-1Rh*	53.91	
Zr-0.25As*	131.27	
Zr-1As	Loss	Disintegration
Zr-0.25Te	19.01	
Zr-1Te	39.09	
Zr-0.25Ge*	43.30	
Zr-1Ge*	202.96	Spalling
Zr-1Ag*	1916.99	
Zr-0.25Ni	32.84	
Zr-1Ni	33.23	
Zr-3Ni*	103.25	

* Specimens showed various degrees of whitening and/or spalling and disintegration; and were removed from further testing.

TABLE V

ALLOYS BEING TESTED IN 900°F STEAM

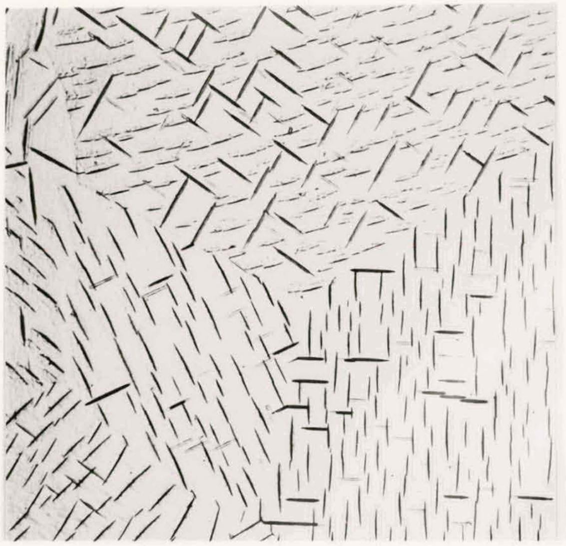
Zr-(0.5, 2, 5, 30)Nb
Zr-(7, 10, 12)Sn
Zr-(0.25, 1, 3, 5, 9)V
Zr-(0.25, 1, 2.5, 4, 6)Sb
Zr-0.25Cu
Zr-(0.25, 1, 3)each Fe, Mo, Co, Pd, Ni

to 680° F water, beta must not transform to omega or the equilibrium beta plus beta prime microstructure.

Quenching studies were carried out on a series of zirconium alloys containing 0.5 - 50 w/o Nb. The compositions of 25% Nb and below contain unidentified "markings" as shown in Figure 9. These platelets have been observed in past investigations and have never been satisfactorily explained. The recent investigation of Lundin and Cox(10) states that the platelet phase is thought to be a metastable transitional phase formed at the monotectoid temperature. At any rate, the 30% Nb alloy did not show these markings after quenching and had a clean, fully-retained beta microstructure as depicted in Figure 10. Since the as-quenched Zr-50Nb alloy was also two-phase (retained beta + beta-prime), the 30Nb alloy appears best suited for this study.

It remains then to determine the stability of retained beta at 680° F. The as-quenched Zr-30Nb alloy was tempered at 680° F, and the hardness was determined at various time intervals. Figure 11 shows the results of this study. Apparently, transformation begins after approximately 60 hours at temperature--hardly sufficient time for determining long-time corrosion resistance of an all beta alloy. For short-time preliminary evaluation, 60 hours would be sufficient. (The transformation causing the large increase in hardness is probably due to presence of the transition phase omega. The completed reaction is $\beta \longrightarrow \omega + \beta \longrightarrow \beta + \beta'$, and the appearance of omega could be detected by X-ray diffraction.)

M. L. Picklesimer at Oak Ridge National Laboratory has done extensive work on delaying the transformation of beta by use of alloy additions. He found that the addition of molybdenum to zirconium-niobium alloys was most effective in delaying transformation. Thus, an alloy Zr-30Nb-5Mo has been prepared and is presently being investigated for use in this study. Chromium-niobium combinations show good steam corrosion properties,(5) and the use of chromium for delaying transformation is being considered. Further, the shape of the time-temperature-transformation diagram is such that higher temperature testing would actually prolong retention of beta.(12) The possibility exists, therefore, that corrosion testing of a retained-beta

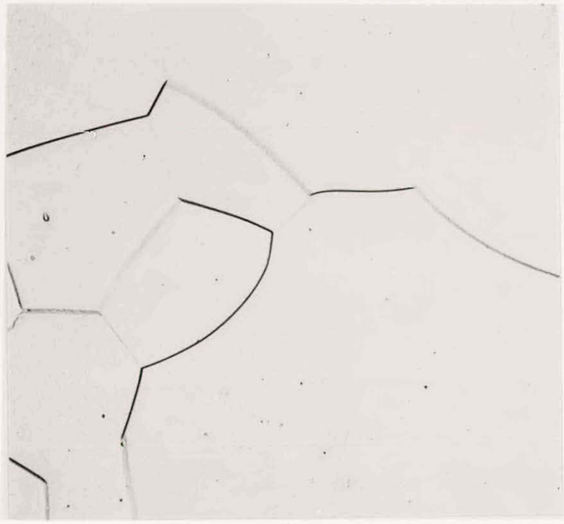


Neg. No. 20591 Mag. X250

Figure 9

Zr-25Nb beta-quenched from 1000° C showing a high density of "markings" in a retained-beta matrix. Markings are possibly transformation products (incomplete).

Etchant: 1 HF, 1 HNO_3, 3 glycerin.



Neg. No. 20590 Mag. X250

Figure 10

Zr-30Nb beta-quenched from 1000° C. Microstructure is fully retained-beta free of "markings".

Etchant: 1 HF, 1 HNO_3, 3 glycerin.

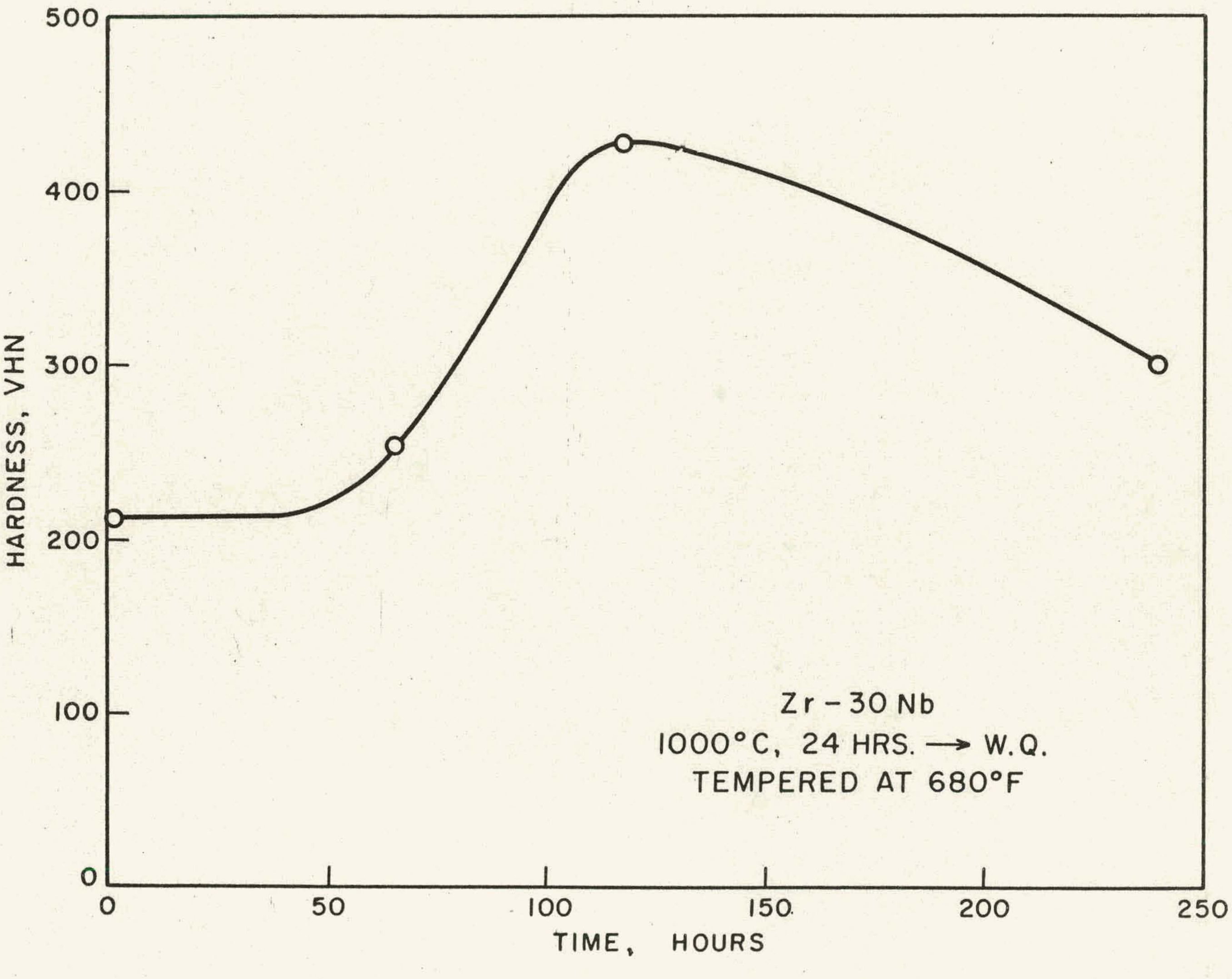


FIG. 11 - HARDNESS vs. TEMPERING TIME FOR Zr-30Nb BETA-QUENCHED FROM 1000°C.

alloy would employ a zirconium-niobium-chromium composition in a high-temperature steam atmosphere.

D. Zirconium Purity

A small quantity of high-purity iodide zirconium (received from Bettis) was arc-melted, and the microstructure of this material appears in Figure 12. Of particular importance for investigation of the effect of zirconium purity on corrosion resistance is the "pepper-like" precipitate which appears to be generally distributed throughout the microstructure. In an investigation by Levinson,(3) five specimens of iodide zirconium were electron-beam melted; four specimens had a microstructure similar to that shown in Figure 12; however, one had exceptionally clean grains and a complete lack of the pepper-like precipitate. The hardness of this specimen was 69 VHN (approximately 20 points lower than the others), but chemical analysis did not reveal any significant impurity differences. Most important, however, this clean, low-hardness, precipitate-free specimen showed enhanced corrosion resistance in a preliminary test.

At the time this electron-beam refining was carried out, the furnace leak rate and atmosphere was not as good, in general, as can presently be obtained.(13) Furnaces are now available which have an exceedingly low leak rate; apparently, the leak rate is a strong factor in the resulting purity and microstructure. Thus, in an attempt to produce extremely clean zirconium, five specimens (100 grams each; four of iodide, one of sponge) have been shipped to Alloyd Research Corporation, Cambridge, Massachusetts, for electron-beam refining in a furnace having an extremely low leak rate. The as-refined material will be examined metallographically, and selected compositions prepared from this refined material will be corrosion tested.

V. DISCUSSION

Although corrosion results are incomplete, a number of general statements can be made concerning results to date. Zirconium-niobium alloys containing relatively small percentages of niobium show attractive corrosion behavior in 680° F water; in 750° F steam, only the Zr-0.5Nb alloy offers promise for further development into a successful alloy. A minimum in the corrosion rate appears to occur (680° F water) at 30 per cent niobium; however,

Neg. No. 20588 Mag. X500

Figure 12
Arc-melted iodide zirconium showing general "pepper-like" precipitate in alpha-prime matrix. Unidentified, black, needle-like markings appear to be mechanical twins. Subgrains are apparent.

Etchant: 1 HF, 1 HNO_3, 3 glycerin.

the weight gain is still comparatively high. Since the nuclear properties of zirconium-niobium alloys are attractive, further work should be done on these compositions for improving corrosion resistance.

Some interesting behavior was noted in the corrosion data for zirconium-tin alloys. In 680°F water, as the amount of tin is increased, corrosion resistance becomes progressively worse. In 750°F steam, however, the trend seems to be reversed. That is, above 3 per cent tin corrosion resistance appears to improve; at compositions of 10 per cent tin and higher, corrosion behavior in 750°F steam may be promising. A number of past investigations(14, 15) have pointed out that the presence of tin in alloys exposed to steam has little or no effect on corrosion resistance. Moreover, at higher temperatures, tin seriously reduces corrosion resistance. In these past investigations, however, a maximum of only 1.5 per cent tin was investigated; from the present data, large percentages of tin appear to improve corrosion resistance at high temperatures rather than adversely affect resistance. In addition, an alloy containing a relatively high percentage of tin would be expected to possess improved high-temperature strength properties.

Vanadium and antimony alloys also showed interesting corrosion behavior. Compositions containing 0.25 and 1 per cent vanadium initially appeared acceptable in 680°F water; however, with higher vanadium contents, corrosion resistance was extremely poor. In steam, a surprisingly low corrosion-rate minimum occurs at 1 per cent vanadium which indicates the possibility for further development to a steam corrosion resistant alloy. Powers and Bibb(16) have pointed out similarities to the present behavior; they observed a binary vanadium alloy to perform well in steam but not in water. Binary compositions containing up to 4 per cent antimony exhibited good initial water corrosion resistance; however, higher percentage alloys were unacceptable. Powers and Bibb(16) have observed similar behavior. In 750°F steam, Zr-0.25Sb was extremely poor, but Zr-1Sb was comparable to Zircaloy-2. As the antimony content increased, weight gain was progressively higher. Since antimony is an alpha-stabilizer, it has considerable attractiveness for development of improved strength, corrosion-resistant zirconium alloys. As previously mentioned, other initial promising compositions are summarized in Tables II, III, IV, and V.

Reduction of impurity content in zirconium and heat treatment are possible means of improving corrosion resistance. In addition to Levinson's(3) cursory corrosion investigation of electron-beam-melted zirconium, further evidence is available that reduction of impurity content will improve corrosion properties. Dalgaard,(17) working with a Zr-2.5Nb composition quenched from 1000° C, observed improved corrosion resistance in an alloy made from crystal bar zirconium as compared to an alloy made from sponge. Furthermore, the time to transition was increased by a factor of 2 to 4. These results are very encouraging; since furnaces are now available for large-scale electron-beam melting, use of highly refined zirconium might be economically feasible.

Heat treatment for the purpose of improving corrosion resistance is certainly economically feasible; however, data on this effect are scattered and not conclusive. By various annealing and quenching cycles, both improvement and impairment of corrosion resistance have been reported. However, no investigation of the corrosion behavior of a fully retained beta alloy has been made. In general, single-phase solid solution alloys exhibit better corrosion resistance than two-phase compositions. It is possible, therefore, that a retained beta alloy would have better corrosion properties than the same composition in the two-phase equilibrium condition. Efforts under the current program are being devoted to studies of heat treatment as well as impurity effects in order to evaluate the magnitude of these factors on corrosion resistance.

VI. FUTURE WORK

Of the six topics listed under "Scope of Investigation" (Section II) the first four can be classified as developmental, whereas the latter two (hydrogen pickup during corrosion and mechanical properties) are considered acceptability tests during the current year. By the structure of this program, corrosion resistance is being used as the initial criterion for acceptance, and work is initially concentrated on the first four topics. After data are accumulated which indicate good alloys, acceptablility tests are initiated. Corrosion hydrogen pickup and mechanical property determinations are recognized as important topics for development of improved alloys. Considerable effort will be devoted to these studies, as development criteria, in future work.

Based on this program structure, work for the remaining period under the current contract, as well as suggested future work based on these results, can be planned. Tests in 680°F water will continue for the purpose of accurately establishing the effect of binary additions on corrosion resistance. Further corrosion data will be obtained for exposure to 750°F steam, and tests at 900°F will be initiated. Work will continue on the effect of zirconium purity and heat treatments on corrosion resistance. As results of longer-time corrosion tests become available and indicate compositions for further alloy developments, mechanical property tests and corrosion-hydrogen pickup determinations will be initiated.

With corrosion data for binary alloys completed, a logical continuation of current studies should concentrate on ternary and higher order alloys. Specifically, six or seven ternary bases would be chosen to which a third element, known to improve corrosion resistance, strength, or hydrogen pickup, would be added. Although data are incomplete, some systems that might be considered for further development could be Zr-Nb, Zr-Sn, Zr-Sb, Zr-V, Zr-Cr, Zr-Ni, and Zr-Mo. The choice of base compositions and ternary additions will also consider such properties as fabricability and neutron absorption cross section. Investigation and screening of ternary compositions should directly lead to successful alloys.

VII. CONCLUSIONS

Experimental work on a program for development of improved zirconium alloys has been summarized for the period April 1, 1960, to January 31, 1961. Corrosion screening tests are being carried out on a large number of binary compositions, and the results obtained are being used for design of ternary and higher order alloys. Due to the large number of alloys under investigation, the wide work scope of this program, and the fact that experimental work is still in progress, no final conclusions can be presented at this time. Results to date, however, indicate that some original concepts used in planning this program are manifested by experimental data. In particular, the encouraging trend in corrosion behavior of relatively high-percentage tin alloys in 750°F steam offers support for investigation of wide ranges of binary systems as well as a study of minor additions to promising ternary and quaternary alloys. By this method, a major improvement over currently available materials (Zircaloy) can be developed. The behavior of particular binary alloys of antimony and vanadium in high-temperature steam is also of possible interest.

Efforts to improve corrosion resistance by alloy development are being augmented by studies of the effects of heat treatment, hydrogen pickup, and impurity contents. In addition, the possibility of improved corrosion properties of a retained-beta alloy are under investigation. Although data for these topics are not complete, current studies indicate that these factors should contribute to the development of superior materials. At the completion of corrosion screening tests, choice of compositions for further development will be indicated by accumulated experimental data. Concurrently, the effects of heat treatment, impurity content, hydrogen pickup, and microstructure should aid in alloy selection. As alloy development efforts include many compositions containing relatively large additions, mechanical properties may be expected to show improvements over current materials.

VIII. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data presented in this report are recorded in ARF Logbooks Nos. C-9748, C-9749, C-9750, C-10612, C-10882, and D-1452.

Personnel contributing to this work are the following:

W. L. Ross	-	Project Technician
F. C. Holtz	-	Group Leader
R. J. Van Thyne	-	Supervisor (early part of program)
D. Weinstein	-	Project Engineer

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

D. Weinstein
D. Weinstein, Associate Metallurgist

FC Holtz
F. C. Holtz, Senior Metallurgist

R. J. Van Thyne
R. J. Van Thyne, Asst. Director
Metals Research

rmh

REFERENCES

✓1. D. Weinstein, R. J. Van Thyne, and D. W. Levinson, "Improved Zirconium Alloys--A Summary of Recent Work in This Field," Interim Report ARF 2198-6, U.S./EURATOM PROGRAM, September, 1960.

2. O. S. Ivanov and V. K. Grigorovich, "Structure and Properties of Zirconium Alloys," Proceedings, Geneva Conference, P/2046, Vol. 5, 1958, p. 34.

3. D. W. Levinson, "Some Experiences With Reactive Metals Melted in High Vacuum, "Proceedings, Conference on Reactive Metals, AIME, 1959, pp. 123-30.

4. J. M. Markowitz, "Hydrogen Redistribution in Zircaloy-2 Under Thermal and Mechanical Stress Gradients," WAPD-TM-171, January, 1959.

5. H. H. Klepfer, "Zirconium Alloys for Steam Service," GEAP-3462, June 24, 1960.

6. S. Kass, "Corrosion Testing of Two Zirconium Alloys," Corrosion, Vol. 16, February, 1960, p. 137.

7. S. Kass, "Corrosion Testing Zircaloy and Hafnium Coupons," WAPD-ZH-25, October, 1960, p. 14; also "Discussion of Corrosion Testing Techniques," ibid, p. 22.

8. B. A. Rogers and D. F. Atkins, "Zirconium-Columbium Diagram," Trans. AIME, Vol. 7, No. 9, September 1955, p. 1034.

9. R. F. Domagala and D. J. McPherson, Discussion of the paper "Zirconium-Columbium Diagram," Trans. AIME, Vol. 8, No. 5, May, 1956, p. 619.

10. C. E. Lundin and R. H. Cox, "The Determination of the Equilibrium Phase Diagram, Zirconium-Niobium," Denver Research Institute, Interim Report No. 1, USAEC, August, 1960.

11. K. Anderko, Unpublished Work done for US/EURATOM PROGRAM at Metallgesellschaft, Frankfurt A. M.

12. R. F. Domagala, D. W. Levinson, and D. J. McPherson, "Special Zirconium Alloys," ARF Project No. B100, Report No. 18, for Oak Ridge National Laboratory, October 15, 1957.

REFERENCES (continued)

13. C. d'A Hunt, Temescal Metallurgical Corporation, Berkeley, California, private communication.

14. S. B. Dalgaard, "The Corrosion Resistance of Zr-Nb and Zr-Nb-Sn Alloys in High-Temperature Water and Steam," CR Met-911, AECL No. 993, March, 1960.

15. J. P. Pemsler, "Corrosion of Zirconium Alloys in 900° and 1000° F Steam," NMI-1235, March 15, 1960.

16. A. Powers and A. Bibb, Knolls Atomic Power Laboratory, Schenectady, New York, private communication.

17. S. B. Dalgaard, Zirconium Newsletter, FD-36-3, July 29, 1960, p. 13.