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SPECIFIC ZIRCONIUM ALLOY DESIGN PROGRAM

First Quarterly Progress Report, February - June 1962

By

H. H. Klepfer

D. L. Douglass

J. S. Armijo

July 1, 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

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FIRST QUARTERLY PROGRESS REPORT

FEBRUARY - JUNE 1962

July 1, 1962

PREPARED FOR THE ATOMIC ENERGY COMMISSION AND EURATOM

by

H. H. Klepfer, D. L. Douglass, J. S. Armijo

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General Electric Company
Atomic Power Equipment Department
Vallecitos Atomic Laboratory
Pleasanton, California

APPROVED BY:

A. N. Holden, Manager
Metallurgy and Ceramics

CONTRIBUTORS TO THE REPORT

Project Scientist	H. H. Klepfer
Task A - Corrosion Mechanism	D. L. Douglass
Hydrogen Overvoltage	S. J. Armijo
Film Stripping	W. E. Urata
Task B - Alloy Design	H. H. Klepfer
Fabrication	K. C. Antony
Statistical Design	D. W. Gaylor
Chemical Analysis	M. E. Urata H. Perine
Corrosion Facility	W. B. Nelson

TABLE OF CONTENTS

	<u>Page No.</u>
Introduction	1
Summary	3
I Task B - The Design of a Zirconium Base Alloy for Steam Service	
Part I - Specifications	
Introduction	4
Requirements	
1. Nuclear Economy	11
2. Low Cost	12
3. Low Susceptibility to Hydrogen Embrittlement	12
4. Usable Long Time Corrosion Rate	22
5. Usable Ductility	34
6. Strength	36
Summary of Specifications	39
References	41
Part II - Selection of Alloying Additions	
Introduction	44
Alloying Elements Eliminated or Chosen on the Basis of the Specifications	45
1. Neutron Economy	46
2. Low Cost	48
3. Low Susceptibility to Hydrogen Embrittlement	56
4. Corrosion	60
5. & 6. Ductility and Strength	68
Alloy Field	71
Alloys for Statistical Analysis of Performance	84
Summary	89
Appendix A to Part II	
Calculations and Assumptions	90

TABLE OF CONTENTS (2)

	<u>Page No.</u>
Results	94
Discussion	95
References	96
II Task A -- Corrosion Mechanism	
Introduction	99
1. Oxide Film Compositions	
Program Description	100
Experimental Program	101
2. Relation Between Film Composition	101
3. Partitioning of Alloy Elements	
Program Description	101
Experimental Program	102
4. Hydrogen Overvoltage	
Program Description	102
Fabrication of Specimens	103
Overvoltage Apparatus	103
Measurement Technique	103
Preliminary Results	105
Significance of Hydrogen Overvoltage	108
Further Work	112
5. Properties of Oxides	
Program Description	112
Experimental Results	113
References	115
III Task B - Program Status	116
IV Technical Liaison	117

ILLUSTRATIONS

Page No.

Part I

Figure 1 - Hydrogen Weight Gain as a Function of Film Thickness	14
Figure 2 - Hydrogen Weight Gain as a Function of Film Thickness	15
Figure 3 - Hydrogen Weight Gain as a Function of Film Thickness	17
Figure 4 - General Form of Hydrogen Solubility in Zirconium Alloys	20
Figure 5 - General Form of Zirconium Alloy Corrosion Curves	23
Figure 6 - Time to Transition to Linear Corrosion Rate	24
Figure 7 - Post Transition Corrosion Rates as a Function of Temperature for Zr-2 and Some Experimental Alloys	35

Part II

Figure 1 - Alloying Elements Eliminated From This Zirconium Alloy Design by Nuclear Considerations Alone	49
Figure 2 - Alloying Elements Eliminated From This Zirconium Alloy Design by Cost Considerations	53
Figure 3 - Alloying Elements Eliminated This Zirconium Alloy Design on the Basis of Corrosion Resistance	62
Figure 4 - Corrosion Weight Gains for Zr-V Binary Alloys in Steam (400°C)	66
Figure 5 - Zirconium-Columbium System	80
Figure 6 - Zirconium-Chromium System	81
Figure 7 - Zirconium-Iron System	82
Figure 8 - Zirconium-Copper System	83

Part III

Figure 1 - Hydrogen Overvoltage Cell	104
Figure 2 - Hydrogen Overvoltage Versus Current Density for Zirconium and Zirconium Intermetallics	106

INTRODUCTION

This is the first progress report under the program which was initiated January 29, 1962 under Contract AT (04-3)-189, Project Agreement 24 as part of the Euratom - USAEC Joint Research and Development Program.

The investigation will explore the design of a zirconium base alloy for application as nuclear fuel cladding for steam service. Both a statistically designed empirical approach (Task B) and a basic approach (Task A) to the alloy design are included in the program.

The first two steps under Task B, establishment of target properties and the selection of the alloy field for study, have been completed and appear as Part I and Part II of the first section of this Quarterly Report. The experimental procedures for the statistical study Part III will be presented as the first section of the next Quarterly Report. Fabrication of the alloys for test is just being completed so that the results of test and their analysis, employing computer programming where necessary, will appear in subsequent progress reports.

An improved understanding of the basic alloying phenomena of zirconium alloys will be developed under Task A, particularly as it relates to the findings from the statistical alloy testing under Task B. Task A is comprised of five experiments directed toward answering these questions:

- a. What is the nature of the protective oxide on a corroding zirconium alloy in terms of chemical composition, permeability to oxygen and hydrogen, mechanical properties, and electrical properties; and how are these properties changed as the alloy content of the metal substrate changes?
- b. What is the role of the intermetallic compounds present as second phases in the metal substrate in determining corrosion hydrogen pick-up through the oxide film?
- c. How do the nature of the oxide films and the role of the intermetallic compounds correlate with the steam corrosion performance of the alloys tested under Task B?

A detailed discussion of the experiments in progress under Task A is given in Section 2 of this Quarterly Report.

Sections 3 and 4 of this report deal with the status of the experimental work, anticipated schedule, and technical liaison.

SUMMARY

A program has been initiated for the design of a zirconium base alloy for application as nuclear fuel cladding for steam service. Specifications have been derived for an acceptable alloy for such service based on considerations of neutron economy, cost, hydrogen embrittlement, corrosion resistance, fabricability, and strength. The selection of the field of alloy compositions having promise for meeting these specifications has been made. Thirty-one alloys whose compositions were chosen from the alloy field have been arc-melted and are being fabricated to sheet. Specimens cut from the sheet will be tested for response to composition. The response parameters will measure corrosion resistance at 300, 400, and 500 C, mechanical properties before and after corrosion exposure, and hydrogen take-up during corrosion. The experiment is designed to permit analysis of the results employing computer programming to determine the optimum composition within the selected alloy field.

Fundamental studies in support of the alloy design have also been initiated. Film stripping techniques have been developed in order to permit studies of the partitioning of alloying element between the corrosion film and the alloy substrate. Hydrogen overvoltage measurements have been made for the intermetallic phases Zr_2Cu , Zr_2Ni , for Zr-90% Nb and for crystal bar zirconium. The diffusion of oxygen in bulk non-stoichiometric zirconium oxide has been measured:

$$D = 0.055 \exp (33,400 \pm 3,100/RT) \text{ for } ZrO_{1.955} \text{ from } 700 \text{ C} - 1000 \text{ C}$$

The activation energy is in agreement with that for parabolic corrosion of zirconium alloys indicating that bulk oxygen diffusion in the corrosion films and not short circuiting diffusion paths are rate controlling. Oxygen diffusion in alloy oxide-doped zirconium oxide is now being studied.

I. THE DESIGN OF A ZIRCONIUM BASE ALLOY FOR STEAM SERVICE

(TASK B - H. H. KLEPFER)

PART I. SPECIFICATIONS

Introduction

Since 1948 when the significant discovery of the low neutron absorption of zirconium was made, considerable effort has been devoted to the development of zirconium alloys for nuclear applications. In the United States, for example, under the auspices of the various branches of the United States Atomic Energy Commission, Zircaloy-2 has become a commercially available specialty material. The physical and mechanical metallurgy of zirconium is well advanced, and practical procedures for the fabrication and joining of alloys are well established. Zircaloy-2 has been widely tested as a cladding for various fuel types including unbonded uranium dioxide fuel elements for water reactors. The limits of utilization of the zircaloys are presently being determined on the basis of basic properties and irradiation experience. In order that the full economic potential of zirconium alloys for nuclear reactor applications can be realized however, further developmental efforts are indicated.

The demands on reactor materials have become, and will continue to become, more severe as the development of economic nuclear power continues. Each successive generation of power reactors specifies longer life, improved neutron economy and higher operating temperatures. Meeting these requirements demands the development of several alternate zirconium alloys designed to meet specific requirements. The requirements for coolant channels or pressure tubes may well be best met by an alloy not suited for thin section fuel cladding. Different reactor designs stress certain requirements above others. The compromises necessary in the course of an alloy design may be decidedly different, depending upon the critical properties in a particular application. The development of special steel compositions to meet specific service requirements is well known.

Examples of different nuclear reactor coolant environments for which zirconium alloy developments have been pursued are given in Table I. The alloys presently most acceptable for service in these environments are

also included in the table.

The development of zirconium-base alloys for organic-cooled reactors has not been particularly successful. This is due to the very rapid hydriding of zirconium in these environments under irradiation by the radiolytic hydrogen produced. Zirconium and all known zirconium alloys are severely embrittled by hydrogen under these conditions. Because of the combination of reasonable strength and low thermal neutron cross section, there are still efforts to use zirconium pressure tubes in organic reactor designs. An aluminum base material would be used as a pressure tube liner. The aluminum base material would give corrosion resistance and resistance to hydrogen embrittlement and the zirconium tube would give the required strength.

The development of zirconium-base alloys for carbon dioxide-cooled reactors was initiated by British investigators and was reported at the 1958 Geneva Conference.⁽¹⁾ Further work on zirconium alloys for carbon dioxide environments has been carried on both in Canada and the United States in support of CO₂-cooled reactor studies. The zirconium alloy containing small amounts of copper and molybdenum first suggested by the British is apparently still the most acceptable of the alloys for the CO₂ service. The corrosion resistance limit of this alloy, however, evidently does not permit its use at the highest temperatures of interest. Reactor operating experience with the zirconium-copper-molybdenum alloy has not been extensive. This alloy is reasonably strong in the temperature range of interest, but is being considered primarily for bonded cladding to fuel elements where the strength requirements of the alloy are not very severe. This is an example of the development of a zirconium alloy in which oxidation resistance is a primary requisite. Hydrogen embrittlement is, of course, no problem in this particular environment.

The development of zirconium-base alloys for sodium-cooled reactor service is, on the other hand, an example of a development in which the primary requirement was high strength. The oxidation behavior of zirconium-base alloys in sodium has been fairly extensively studied, and

TABLE INUCLEAR ENVIRONMENTS IN WHICH ZIRCONIUM ALLOYS ARE OF INTEREST

<u>Coolant</u>	<u>Temperature Range of Interest</u>	<u>Pressure Range of Interest</u>	<u>Alloy Presently Most Acceptable</u>
Organic	260 C - 425 C	Near Atmos.	None
Carbon Dioxide	400 C - 600 C	300 psi - 1000 psi	Zr + 1 w/o Cu + 1.5 w/o Mo
Sodium	500 C - 850 C	Atmos.	Zr + 1.25 w/o Al + 1 w/o Sn + 1 w/o Mo
Water	260 C - 360 C	Saturation	Zircaloy-2 (Zr-4)
Steam	260 C - 600 C	500 psi - 1500 psi	Zircaloy-2

apparently the oxidation resistance depends more on the oxygen content of the sodium coolant than upon the alloy content of the zirconium alloy. The alloys most acceptable at this time for the sodium-cooled service contain large amounts of alpha-stabilizing elements such as aluminum and tin and also contain beta-stabilizing elements which promote sluggish transformations of beta zirconium to coherent precipitate phases in an alpha matrix. The problem with these alloys is that along with high strength they exhibit low ductility & marginal fabricability. An additional problem, unique to this application, is the reaction between the cladding and the fuel at the higher temperatures of interest. Development of high strength zirconium alloys for sodium-cooled reactor service is continuing to be supported by the sodium-cooled reactor projects. Corrosion resistance in sodium is apparently acceptable for most of these high strength alloys. The strength levels being achieved in these alloys are comparable to that which could be expected as the optimum. It is not anticipated that large strides will be made in developing stronger zirconium alloys than those which have been reported.⁽²⁾ Greater ductility and fabricability at these high strength levels will undoubtedly be the target for further development of zirconium alloys for sodium-cooled reactor service.

The most successful zirconium alloys have been those used in water-cooled reactor environments. The development of the Zircalloys for water reactor service has been described in detail.^(3,4) The Zircalloys are examples of zirconium alloys in which an optimum combination of strength (due to the tin alloy addition) and corrosion resistance (due to the transition metal alloy additions) has been achieved. The performance of these alloys in actual water-cooled reactor service has been reviewed quite recently. Lustman, et al⁽⁵⁾ have described the good performance of Zircaloy-2 in the Shippingport Reactor; Perryman⁽⁶⁾ has discussed the use of Zircaloy-2 in the CANDU reactor; and Klepfer⁽⁷⁾ has discussed the utilization of Zircaloy-2 in boiling water reactor environments. Zircaloy-2 clad fuel elements have performed well in both the Shippingport Reactor and the Dresden Nuclear Power Station. The strength of these

alloys in water reactor service has been found quite adequate. Usable ductility has been found in these alloys after rather long time radiation exposures. The effect of irradiation on the corrosion of these alloys has been reported only very recently. Krenz⁽⁸⁾ indicates that radiation increases the rate (evidently pre-transition rate) of corrosion by a factor of about two. Nelson and Parker⁽⁹⁾ and Cox⁽¹⁰⁾ report that the post-transition corrosion rate of Zircaloy-2 may be increased by as much as 4 to 8 times under neutron radiation at high flux levels (about 10^{13} nv). In spite of this increase in corrosion rate, all three investigators agree that the percentage of corrosion hydrogen that finds its way into the underlying metal is not increased by radiation.

It has been found, in spite of radiation-increased corrosion, that the use of the zircaloys for thin-walled cladding (expected to perform for about three years) and for thick-walled pressure tubes (expected to perform for 10 to 20 years) is, in fact, quite acceptable in water at 260-300 C. There is still some concern that Zircaloy-2 may not be acceptable for long time service (10-20 years) for thin-walled flow channels where the corrosion hydrogen embrittlement may be a problem. The Zircaloy-4 composition (where nickel has been removed from Zircaloy-2 and the iron content increased) may, however, perform satisfactorily even in this case since the percentage of the corrosion hydrogen which finds its way into the underlying metal is evidently significantly lower than it is in the case of Zircaloy-2. It is, therefore, questionable whether a concentrated alloy development effort for zirconium alloys for water service is required or necessary. More important in the case of zirconium alloys for service at 260-300 C in water is the establishment of much lower costs for mill product fabrication. For any composition, high mill product costs, characteristic of zirconium alloys, are related to low material yield and the high cumulative value of the rejected material. Stringent quality control at certain points is necessary in nuclear grade mill products and, in part, accounts for the low material yield. Thus, both realistic quality control cost reductions and fabrication process innovations are

required in order to reduce mill product costs.

In the case of steam environments it would appear that the full potential of zirconium-base alloys has not yet been realized. No completely acceptable alloy has been brought into full development for steam service. The Zircalloys have only a limited range of temperature in which they are technically acceptable in steam. Zircaloy-2 is limited by corrosion hydrogen embrittlement at temperatures on the order of 400 C and above. Zircaloy-4, on the other hand, with its lower hydrogen take-up, is limited by corrosion penetration and by corrosion product spalling and, in fact, ultimately hydrogen embrittlement at elevated temperatures in steam. The offending alloying element in the case of the Zircalloys is apparently tin. Zirconium-tin binary alloys are known to corrode very rapidly and disintegrate in a short time in high temperature steam. The early work of Pemsler⁽¹¹⁾ on zirconium alloys containing additions of chromium, iron, and nickel is perhaps the most significant among the studies of zirconium alloys for steam service. These studies, however, did not give primary emphasis to the problem of corrosion hydrogen take-up and corrosion hydrogen embrittlement of the alloys.

The problem of the design of a zirconium alloy for steam service in nuclear applications is the one to which our present study will address itself. The alloy development, then, that will be considered in the remainder of this discussion is one for application for thin sections such as those in fuel element cladding where resistance to corrosion and degradation of mechanical properties during corrosion are the critical requirements. Good fabricability and high ductility are also required. This alloy, which would not require high strength, would have application for supported or bonded fuel cladding, or perhaps for co-extruded protective cladding on high strength zirconium alloys. Such an alloy would be useful as cladding material for unbonded UO_2 fuel elements designed to rely on the UO_2 in the fuel tubes for the support of the cladding which would otherwise collapse due to the reactor coolant pressure. Designs of this kind are, of necessity, being developed for very thin, stainless

steel-clad, UO_2 fuel elements. This low strength, high ductility alloy also holds some promise for greater fabricability and, thus, lower mill conversion costs.

The requirements which must be met in this design of a zirconium-base alloy for steam service for application in fuel element cladding of the non-self-supporting type are listed below:

1. Neutron economy.
2. Low cost.
3. Low susceptibility to hydrogen embrittlement.
4. Usable corrosion resistance.
5. Usable ductility.
6. Strength approximately equal to that of zirconium sponge.

Each of these requirements will be discussed and practical limits will be developed. Finally these limits will be combined to give a description of the quantitative targets for an alloy acceptable for the service in steam which has been described. It should be emphasized that the specifications which will be developed are those for an alloy intended for this one specific application which we are discussing. The development of these specifications will conclude Part I of this study.

Part II will develop the selection of alloying additions in light of the specifications put forth here in Part I. Part III will give the details of the experimental program to be carried out including the statistical choice of compositions, the choice of starting materials, fabrication procedure, testing methods, expected data, methods of data reduction, and the method of statistical analysis of the results which will be used to determine the optimum composition within the alloy field selected. Finally, the method of comparison of the properties of the optimum composition within the alloy field against the specifications will be outlined to conclude Part III. Subsequent parts of the study will report the experimental results.

Requirements

1. Nuclear Economy

The incentive for using an expensive reactive material such as zirconium as the alloy base for materials to be used in nuclear applications derives entirely from the low thermal-neutron capture cross section of the zirconium atom. Thus, in the design of any alloy to be used in nuclear applications it is essential that the alloying elements do not nullify this intrinsic advantage of the zirconium. The addition of high thermal-neutron capture cross section elements must not cause a significant increase in the macroscopic capture cross section of the resulting alloy. One way to put practical limits on the alloying additions which would be tolerable with respect to neutron economy would be to limit the increase in fuel enrichment required by a given alloying addition. A calculation of this type has been made using the Dresden Nuclear Power Station Core as an example. The limit taken was the amount of various alloying element additions which would lead to no more increase in enrichment than 0.05 percent U-235. This percentage increase in the U-235 enrichment of this amount is real. However, in practice the actual feasible control of enrichment in fuel is on the order of ± 0.10 percent U-235. All elements are included in the calculations (which will appear in the Appendix of Part II of the present study). We will accept, then, as one of the specifications for this study of the design of a zirconium base alloy for steam service the requirement that alloying additions to the core would not cause an increase in required enrichment of more than 0.05% U-235 as a maximum in a core having the general nuclear physics parameters of the Dresden Nuclear Power Station. We will furthermore calculate the actual macroscopic cross sections of the alloys to be studied and compare these with that of Zircaloy-2.

2. Low Cost

A major problem in the utilization of zirconium base alloys is their high cost. The competitive position which must be taken by the zirconium alloys will set a practical limit on the cost which any new alloy could have. It would seem reasonable that unless some very large advantage could be shown for a new zirconium alloy, that its cost should not exceed that of Zircaloy-2. In the design of a zirconium alloy for steam service we would be able to allow some margin of increase in cost over Zircaloy-2 since we have discussed that we would expect it to perform acceptably over a higher temperature range than that for Zircaloy-2. However, a large increase would not be permissible since it would severely penalize the zirconium alloy with respect to the use of other non-zirconium base alloys in the same application. We will then accept as a practical limit for the design in this study that the alloying additions will not result in cost increases due to increased cost of fabrication, increased cost of the alloying material, increased difficulty in the control of the alloying elements during melting, or due to any other factor which would add more than 5% to the cost now prevalent for Zircaloy-2 tubing. This figure is admittedly somewhat arbitrary, but it will become clear as this design develops that the alloys which we are actually considering will stay well within this limit, and in fact, should show no increase in cost over that for Zircaloy-2. It is clear that changes in Zircaloy-2 costs must be taken into account in the final assesment of an alloy with respect to this specification.

3. Low Susceptibility to Hydrogen Embrittlement

Corrosion hydrogen embrittlement of zirconium alloys may be the limiting factor in their use in nuclear reactors as we have discussed above in the case of the zircaloys in steam. This problem has been recognized for some time and several reviews, notably

notably that by Bieffer, Howe, Sawatsky and Krenz,⁽¹²⁾ have discussed various aspects of the problem. We have been re-examining a number of zirconium alloy compositions to determine if improvements in susceptibility to corrosion hydrogen embrittlement might be found through alloying.

In the course of this re-examination we have noted that the following factors determine embrittlement due to corrosion hydrogen:

- a. Total hydrogen made available by corrosion which is determined by the corrosion resistance of the alloys. Corrosion resistance will be discussed separately in the next section under the requirement for corrosion resistance.
- b. Total hydrogen weight gain in the underlying alloy which is determined by the percentage of the corrosion hydrogen passing through the protective oxide film. The dependence of the percentage of the corrosion hydrogen passing through the protective film on the film thickness was first studied by Cox.⁽¹³⁾ He found that in steam the zirconium alloys showed a high initial rate of hydrogen absorption in the thin film region (less than 10 md/dm^2) followed by a low percentage hydrogen pickup at intermediate film thickness, and then a very high rate of pickup at thickness in excess of the thickness at which a transition in the kinetics of corrosion is observed. The results of experiments done in steam in our laboratory⁽¹⁴⁾ do in fact support this contention as the typical curves drawn in Figure 1 show. (However, in water at 680° F this was never observed in 25 different alloys, even though there was a transition in the corrosion rate. Figure 2 is an example of the water curves. In the initial thin film region a high rate of pickup is observed. The slope for the normal film thicknesses for various binary systems tested in water is shown in Table II.) A second point examined in our experiments was the effect of intermetallic compounds on the

Figure 1. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

Figure 2. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

hydrogen take-up. It has been postulated that the inter-metallics play an important role in governing the percentage hydrogen take-up. The zirconium-chromium, zirconium-vanadium, and zirconium-antimony, and zirconium-iron systems all show limited solid solubility (less than about 0.5 weight percent) and intermetallic compounds. However, no effect of increasing alloy content (increasing volume percent intermetallic) on the hydrogen weight gain versus film thickness curves was observed -- with one exception, iron binaries. The curves in Figure 3 show this effect at 750 F for iron binaries. Note that in Figures 1 and 2 no such composition dependence is observed. It appears from all of the data available that in steam the percent of corrosion hydrogen passing through thick, post-transition films will vary greatly with alloy content, but probably cannot be expected to be below about 10-15% which is the lowest that has been observed in steam (columbium and vanadium binary alloys at 750 F in steam). More typical values for the percentage hydrogen passing through thick corrosion films would be on the order of 25-35%.

c. Solubility for Hydrogen in the Alloy

No systematic study of the effect of alloying elements on the solubility for hydrogen in zirconium has been reported. (19) However, the solubility is known for hydrogen in Zircaloy-2. Brown and Hardie⁽¹⁵⁾ have reported that oxygen increases the solubility for hydrogen in zirconium slightly. Furthermore, Hardie has found that columbium additions increase the solubility for hydrogen in zirconium alloys. This increase for a 2 w/o Nb alloy was to 540 ppm at 300 C; Zircaloy-2 would have a solubility of about 100 ppm at this temperature. In our early studies we looked for metallographic evidence for increases in solubility upon the addition of a wide

Figure 3. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

TABLE II

PERCENTAGE HYDROGEN TAKE-UP IN THICK FILMS AT
360 C IN STATIC AUTOCLAVE WATER TESTS

<u>Alloys (nominal composition)</u>	<u>Slope of ΔW Hydrogen vs ΔW Oxygen</u> <u>Curve for Films Thicker than 10 mg/dm²</u>
Zircaloy 2	~ 25%
1.0, 1.5, 3.5 Nb	~ 12%
0.2, 0.5, 1.0, 1.5, 3.0 Cr	10%
0.2, 0.5, 1.5, 2.0, 3.0 V	4.3%
0.2, 0.5, 1.5, 2.0, 3.0 Sb	< 1.0%

variety of alloying elements. We saw none with the exception of additions of columbium.^(17,18) From these considerations it would appear that the practical upper limit for solubility in hydrogen is still quite low (and is suggested here in Figure 4 which combines the data of Sawatsky⁽¹⁹⁾ and those of Hardie⁽¹⁶⁾ and our metallographic observations.⁽¹⁸⁾

d. The Effect of Hydrogen in the Alloy on Ductility

The fact that hydride precipitation would give rise to a decrease in ductility of zirconium was first reported by Mudge⁽²⁰⁾ in studies concerning the impact energy absorption in zirconium alloys. The effect of hydride precipitate on the tensile properties of Zircaloy 2 was studied in detail by Burton.⁽²¹⁾ He found a gradual embrittlement, i.e. decrease in ductility, with increasing hydrogen content. The effect of the orientation of the hydride platelets in a zirconium sample with respect to the direction of mechanical test has been found to have an important influence on the magnitude of the loss in ductility for a given amount of hydrogen.^(22,23) An order of magnitude difference in the embrittlement due to a given amount of hydrogen has been found in zirconium-columbium alloys where there is a difference in the morphology of the hydride precipitate.⁽¹⁸⁾ If the hydrogen is present as small isolated clusters of hydride precipitate, there is less loss in ductility at the same hydrogen content than there is when the hydride is present as well-distributed, thin platelets, within the microstructure.

The exact limits for hydrogen in zirconium alloys in the practical sense has been considered by a number of investigators. The earlier studies⁽¹²⁾ took as a limit the absence of any hydride precipitate at the service temperature. In the case of Zircaloy-2 for water reactor service this imposed a limit of about 100 ppm hydrogen. This limit has sub-

Figure 4. GENERAL FORM OF HYDROGEN SOLUBILITY IN ZIRCONIUM ALLOYS. DATA OF SAWATSKY FOR Zr-2.

sequently been found to be conservative and later studies, for example those of Canadian⁽⁶⁾ and British⁽¹⁰⁾ workers, have indicated that the limit may be as high as 500 to 700 ppm. In fact, when the combined effect of radiation damage and hydrogen embrittlement is considered, the data of Yeniscavich et al⁽²⁴⁾ indicate that in irradiated Zircaloy-2, (high in nickel) there is no effect of hydrogen up to 500 ppm on ductility. An examination of the phase diagram for zirconium and hydrogen indicates that a complete grain boundary network of the brittle zirconium hydride phase would be expected at about 1500 ppm hydrogen. Our metallographic studies indicate that this is true. When this amount of hydrogen is present in the zirconium, true brittle behavior is found; even the tensile strength is decreased and ductility falls to a very low value. (See Ref. 21 and Rösler's tensile data, Ref.25). Therefore, for the purposes of this study, 1500 ppm hydrogen in excess of the solubility limit will be taken as a definite limit for permissible accumulated corrosion hydrogen during service. Obviously the lower the hydrogen content the more desirable a candidate alloy will be.

In order that all of the factors which we have listed above are integrated and that the actual embrittlement is measured directly, an impact test which we have developed⁽²⁶⁾ and tensile tests will be performed on all corroded specimens. Based on our experience an alloy having a tensile ductility of at least 10% reduction in area and a sheet-impact test energy-absorption value of at least 8 ft-lbs at the service temperature would be acceptable (regardless of its hydrogen content).

Service conditions are defined for the purposes of this study by the exposure of a 25 mil wall tube corroding on one side for three years at the highest temperature consistent with meeting the corrosion specification given in the following section.

The limitations or specifications on hydrogen content are not completely independent of the corrosion of the alloys as we have indicated above. Under the next section we will come back again to the importance of the hydrogen specification and how it relates to the corrosion specification.

4. Usable Long Time Corrosion Rate

Since the potential nuclear application for the alloy which we are studying here will include service lifetimes of perhaps 3 years for cladding, ten years for flow channels, and as long as 20 years for some reactor components, it is necessary to examine the form of the corrosion weight gain versus time curves at long times. Typical corrosion kinetics curves for zirconium alloys are shown in Figure 5. It should be noted that the times to the transition from approximately parabolic corrosion kinetics to the linear rate of corrosion decreases with increasing temperature as shown in Figure 6. At all but the lowest temperatures of interest this time to transition will be shorter than the service lifetime in even the shortest service lifetime case. It should be noted that the linear post-transition corrosion kinetics curve can be extrapolated to intersect the origin so that post-transition corrosion rates, the ones of real interest in writing specifications for design of a zirconium alloy, can be calculated from the post-transition corrosion phenomenon. Three aspects of the corrosion must be considered in determining a specification to be met by a zirconium alloy designed for nuclear service. These are: (a) corrosion penetration (corrosion loss of wall thickness), (b) corrosion product lost to the system, and (c) corrosion hydrogen production.

a. Corrosion Penetration

A corrosion allowance of 10% of the component wall thickness is not unreasonable. Thus a 3 mil corrosion tolerance for a 30

Figure 5. GENERAL FORM OF ZIRCONIUM ALLOY CORROSION CURVES. DATA FOR Zr-2.

Figure 6. TIME TO TRANSITION TO LINEAR CORROSION RATE. DATA FOR Zr-2.

mil fuel cladding wall might be reasonable and thus a tolerable corrosion rate of 1 mil per year ($1.67 \text{ mg/dm}^2/\text{day}$ (mdd)) would be acceptable for a 3 year service life. Furthermore, a 20 mil corrosion allowance on a heavy, 200 mil-wall, pressure tube would also be tolerable and this would again set a corrosion rate limit of 1.67 mdd. Actually it is not inconceivable that corrosion tolerances 2 to 3 times this high might be allowed for certain components, but limits of 4 to 6 mdd must be considered a maximum for corrosion penetration and corrosion loss of wall thickness, since this would mean designing with a 40-60% corrosion allowance on thickness.

b. Corrosion Product Loss to the System

For a shorter time service at very low temperatures, very low weight gains in fact are experienced in service and there is no problem with the tight, black, adherent corrosion film on the Zircalloys with respect to corrosion product loss to the system. However, for higher temperature steam service and for longer time service at low temperatures we may find that there is some corrosion oxide loss to the high velocity coolant system. In steam and water this corrosion product would be expected to be insoluble in the coolant stream. Some filtration of this corrosion product could be affected but there would also be an activation of the zirconium and alloying elements in the neutron flux and some plating out of this activated corrosion product on the circulating system -- pipes and heat exchangers -- or in the direct cycle steam case, plating out of the activated corrosion product in the turbine itself. We have studied over 130 different zirconium alloys after 3000 hours in steam at 750 F and after 1000 hours in steam at 900 F, and we have found no alloy which had a black, tightly-adherent film at weight gains above about 500 mg/dm^2 . In static autoclave tests much higher

weight gains have been measured but the corrosion product is not all adherent. In high velocity coolants certainly some or all of this corrosion product could be lost to the system. On the average, however, the rate of corrosion product loss to the system will not exceed the long-time, post-transition corrosion rate for the particular alloy in question. Some support of our contention that corrosion product loss to the system is to be expected at weight gains at least as low as 500 mg/dm^2 is found in the recent work of Pemsler.⁽²⁷⁾ He finds the onset of cracking in the films at elevated temperatures (700 C to 750 C; 1292 F to 1382 F) to be at about $500\text{-}600 \text{ mg/dm}^2$. For three year service life applications, 500 mg/dm^2 limits the post-transition corrosion rate which is tolerable to 0.5 mdd. For 20 years service this rate would cause spalling at an average rate of no greater than 0.5 mdd over 17 years. Actual system design would determine if these are tolerable limits. Assuming an insoluble corrosion product and assuming plating out on the piping and heat exchanger like that of other crud found in boiling water reactor systems, this 0.5 mdd rate would lead to an estimated radioactivity level about like that in water cooled reactors, and would probably be tolerable.⁽²⁹⁾ One exception to the observation of some corrosion product loss to the system at 500 mg/dm^2 which gives some hope of relaxation of this limit was the observation of Douglass⁽²⁸⁾ that a zirconium-columbium-chromium alloy had a black adherent film at a weight gain of 3000 mg/dm^2 . This relaxation would set a corrosion specification of 3 mdd. The problem of activity level from oxide loss to a nuclear system has not been studied in detail and it is conceivable that new methods of dilution, prevention of crud deposition, or relaxation in reactor circulating system accessibility could relax the tolerable corrosion rate

restriction further. The maximum tolerable rate of oxide loss to the system is not likely to exceed 5 mdd, however.⁽²⁹⁾

Thus far we have not considered the effect of neutron and gamma radiation on corrosion rates. The effect of radiation on corrosion rates of Zircaloy-2 has been reported within the last year. The effect has been reported to be an increase of a factor of 2 by Krenz⁽⁸⁾ and an increase in the rate of corrosion of at least 4.3 according to Nelson and Parker.⁽⁹⁾ The latter have noted an early onset of transition in a neutron radiation flux on the order of 10^{13} nv. (It must be considered possible that this increase may be due to the presence of a heat flux accross the cladding and perhaps due to the chemical impurities in the coolant or crud.) Cox⁽¹⁰⁾ also reported early transition and a corresponding increase in the post-transition corrosion rate in isothermal coupon studies. He estimates the effect of radiation to increase corrosion rate by a factor of eight. Pressurized water reactor studies have not shown any increase of corrosion due to the radiation; at least it has not been reported. Thus, we find ourselves in the situation where we would anticipate that the radiation might increase the rate of corrosion in service by anywhere from 1 to 3 times. This means that the limits which we are deriving here must be decreased by a factor as large as 8 to take into account the acceleration due to radiation. To illustrate the interplay of these factors, note that if the most conservative factor for the effect of radiation, eight, is taken and no metal loss is allowed to the system, then the most conservative specification for out-of-reactor performance would be 0.06 mdd. If the most liberal penetration and metal-loss-to-the-system allowances are taken and no increase in corrosion due to radiation is taken, then the most liberal specification for out-of-pile performance would

be 5 mdd. Obviously the effect of radiation on corrosion is a very critical factor and one which is not well known. The effect may also be different in different environments and may not be quantitatively the same for all alloys.

Before choosing a specification, it is necessary to consider the third aspect of the corrosion phenomenon which is the corrosion hydrogen production.

c. Corrosion Hydrogen Production

The limits of tolerable corrosion rates which are determined by the hydrogen embrittlement involve a number of factors including, as we have discussed, the solubility for hydrogen, the amount of hydrogen precipitate necessary to cause brittle behavior, and, of course, the percentage of the corrosion hydrogen that finds its way into the underlying metal. These various factors are related in Tables III, IV, and V as examples.

In Table III we have taken the hydrogen solubility data for Zircaloy-2⁽¹⁹⁾ and the grain boundary network limitation on ductile behavior at 1500 ppm in excess of the solubility limit, and have assumed in this case the maximum for hydrogen take-up, 100%. When this is done, we then consider two different service lives for a specific case; that is, the 25 mil zirconium wall tube corroding from one side (which is equivalent to a 50 mil sheet corroding on both sides) for 3 year and 20 year service lives. We also note that the tolerable corrosion rate for 20 year service would be roughly the same as that for 3 year service if the wall thickness were increased by 6.6. Furthermore, we have calculated in the Table the tolerable corrosion rates for 3 different possible factors for the effect of radiation on both 3 year service and 20 year service. It will be noted in this case the limits for acceptable corrosion

TABLE III

MAXIMUM ACCEPTABLE CORROSION RATES ASSUMING Zr-2 SOLUBILITY,
100% H₂ PICK-UP AND GRAIN BOUNDARY NETWORK OF HYDRIDE AS LIMITING

Operating Temp.	Rt	300	400	500	600 C
Solubility	8	119	291	604	1070 ppm
G. B. Network(1500+Sol.)	1508	1619	1791	2104	2570 ppm
Equivalent ΔW @ 100% H ₂ Pick-up for 25 mil tube corroding one side	360	427	473	550	678 mg/dm ²
Limit ΔW_0 - No radiation for 25 mil wall tube corroding one side					
3 year service	0.33	0.39	0.42	0.50	0.62 mg/dm ² /day
20 year service	0.049	0.058	0.065	0.075	0.093 mg/dm ² /day
(roughly same as 3 year if tube wall 6.6 x 25 mils)					
Limit ΔW_0 in out-of-pile test to allow for radiation increase in post-trans. rate of:	2.0x	0.16	0.19	0.21	0.25 0.31 mg.dm ² /day
	4.3x	0.077	0.091	0.098	0.12 0.14 "
(3 yr. service for 25 mil wall <u>corroding</u> <u>one side</u>)	8.0x	0.041	0.049	0.052	0.062 0.072 "
(Roughly same as 3 yr. if tube wall 6.6 x 25 mils)					
(20 yr. service for 25 mil wall <u>corroding one side</u>)	2.0x	0.025	0.029	0.032	0.037 0.046mg/dm ² /day
	4.3	0.011	0.013	0.015	0.017 0.022 "
	8.0x	0.006	0.007	0.008	0.009 0.012 "

TABLE IV

MAXIMUM ACCEPTABLE CORROSION RATES ASSUMING Zr-2 SOLUBILITY,
10% H₂ PICK-UP, AND GRAIN BOUNDARY NETWORK OF HYDRIDE AS LIMITING

Operating Temp.	Rt	300	400	500	600 C	
Solubility	8	119	291	604	1070	ppm
G.B. Network(1500+Sol.)	1508	1619	1791	2104	2570	ppm
Equivalent ΔW_o @10% H ₂ Pick-up for 25 mil tube corroding on one side	3600	4270	4730	5500	6780	mg/dm ²
	(Here oxide spalling to system may limit)					
Limit ΔW_o No radiation 25 mil wall tube one side or 50 mil sheet both sides						
3 yr. service	3.3	3.9	4.2	5.0	6.2	mg/dm ² /day
20 yr. service	0.49	0.58	0.65	0.75	0.93	
Limit ΔW_o in out-of-pile test to allow for radia- tion increase in post- transition rate of:	2.0x	1.6	1.9	2.1	2.5	3.1 mg/dm ² /day
	4.3x	0.77	0.91	0.98	1.2	1.4
3 yr. service for 25 mil wall corroding on one side	8.0x	0.41	0.49	0.52	0.62	0.72
20 yr. service for 25 mil wall corroding on one side	2.0x	0.25	0.29	0.32	0.37	0.46 mg/dm ² /day
	4.3x	0.11	0.13	0.15	0.17	0.22
	8.0x	0.06	0.07	0.08	0.09	0.12

TABLE V

MAXIMUM ACCEPTABLE CORROSION RATES ASSUMING MAXIMUM REASONABLE
SOLUBILITY, 10% H₂ PICK-UP, AND GRAIN BOUNDARY NETWORK OF HYDRIDE AS LIMITING

Operating Temp.	Rt	300	400	500	600 C	
Solubility	483	594	766	1179	1645 ppm	
G.B. Network	1983	2094	2266	2679	3145 ppm	
Equivalent ΔW_o @10% H ₂ pick-up for 25 mil wall corroding on one side	4820	5530	6000	7000	8300 md/dm ²	
(Here oxide spalling to system may limit)						
Limit ΔW_o No radiation for 25 mil wall corroding on one side						
3 yr. service	4.5	5.0	5.5	6.4	7.6 mg/dm ² /day	
20 yr. service	0.66	0.76	0.82	0.96	1.1	
Limit ΔW_o in test out- of-pile to allow for radiation increase in post-transition rate of:	2.0x	2.2	2.5	2.7	3.2	3.8 mg/dm ² /day
3 yr. service for 25 mil	4.3x	1.0	1.2	1.3	1.5	1.8
wall corroding on one side	8.0x	0.56	0.62	0.69	0.80	0.95
20 yr. service for 25	2.0x	0.33	0.37	0.40	0.48	0.57 mg/dm ² /day
mil wall corroding on	4.3x	0.15	0.18	0.19	0.22	0.27
one side	8.0x	0.084	0.092	0.10	0.12	0.14

rate in out-of-pile tests allowing for a radiation-caused increase in corrosion would be as low as 0.07 mdd for three years service for this wall thickness, and as high as 0.62 mdd assuming no radiation-caused increase in corrosion. With these assumptions, essentially the worst case assumptions, it will be noted that the corrosion hydrogen limitation is about the same as the limitation we derived for corrosion penetration and corrosion metal loss to the system using the most conservative assumption about the increase in rate of corrosion due to radiation and the conservative assumptions about metal loss. If the more liberal assumptions are made about the effect of radiation and more liberal tolerance for penetration metal loss were used, then we find that the hydrogen embrittlement would be the limiting case at 0.62 mdd.

In Table IV we have used the same assumptions except in this case we have assumed the lowest reasonable pick-up of the hydrogen, 10%. In this case it appears that with low hydrogen pick-up the metal-loss-to-the-system and the penetration by corrosion into the wall is the limiting case, not hydrogen pick-up. As we pointed out before, a thick-wall, 20 year service would have roughly the same limits in terms of hydrogen.

In Table V we have used the most liberal assumptions about what might be conceivable for an alloy for hydrogen solubility (estimated from our metallographic examinations of the 5% columbium alloys) and the lowest reasonable hydrogen pick-up of 10%. In this case it is quite clear again that at least for temperatures of 300 C and above the limit is imposed by corrosion penetration and corrosion metal-loss-to-the-system and not be hydrogen embrittlement. Assuming the high conceivable solubility limit, we find that the hydrogen embrittlement becomes the limiting factor at hydrogen pick-up

fractions (for thick films) on the order of 20-25 percent. We have used in these calculations the simple assumption that the hydrogen take-up is a linear fraction of the corrosion weight gain. This is not quite so. The actual form of the curves was first studied by Cox⁽¹³⁾ and some of our data for different alloys are given in Figures 1, 2, and 3 in this report. We have therefore purposely used the 100% and 10% (experimentally observed) cases for simplification. Our conclusions in the 10% pick-up case will not be changed by the pick-up of 30-40 ppm hydrogen in the thin film region (which we did not take into account).

From the above discussion and examples of the relation between solubility, percent hydrogen take-up, radiation, and corrosion per se, it is obvious that no certain statement can be made about which factor will limit the acceptable performance of any particular alloy. Thus, all factors must be considered in the alloy design.

In our judgement an ex-reactor test corrosion specification for the zirconium alloy design for steam service should be 1 mg/dm²/day. This specification will give no problem with metal penetration, that is, loss of wall thickness due to corrosion if the more liberal allowances for corrosion are accepted and if the actual effect of radiation on the corrosion of the alloys developed is not to increase corrosion by more than a factor of four. This specification would require that the metal loss to the system could be tolerated at somewhat higher levels than are now anticipated but not higher than the conceivable limits we have set, again allowing a factor of 4 increase in corrosion. This specification will also be tolerable with respect to corrosion hydrogen embrittlement, at least at the higher temperatures of service which are of interest. Note that this specification of 1 mdd is a specification for acceptability in

corrosion rate in out-of-reactor test. The actual corrosion rate in-reactor would be expected to be about 4 mdd on the basis of the assumptions we are making. It is recognized that a number of assumptions have been made in setting this as an acceptable specification. However, when this specification is compared to the performance of the most acceptable present zirconium base alloy and the best experimental alloy which we have observed (Figure 7), it will be seen that 1 mdd is a rather challenging target. Examination of Figure 7 reveals that the design problem involves improving the corrosion resistance greatly over that of present zirconium alloys at elevated temperatures in steam. However, in attempting to get this improvement it is permissible to allow considerable relaxation in performance in low temperature steam over that of the zirconium alloys presently in use, the Zircalloys.

5. Usable Ductility

The requirements for ductility in the design of a zirconium alloy for steam service as free standing or non self-supporting fuel cladding, comes primarily from the requirements for fabricability rather than for service. During actual service, radiation damage and hydrogen take-up will lower the ductility from that which was present in the initial material during fabrication. It has been found under irradiation that the elongation to failure may reach the rather low values of 5 to 10% elongation to failure but that reduction in area, a better measure of the ductile behavior of material, is not adversely affected.⁽⁵⁾ Furthermore, the effects of hydrogen and of radiation do not appear to be completely additive and ductile behavior is characteristic of zirconium base materials which have been irradiated up to 6×10^{21} nvt. In fact, it has been found that materials which have high initial ductility reach about the same final levels of ductility after radiation as

Figure 7. POST TRANSITION CORROSION RATES AS A FUNCTION OF TEMPERATURE FOR Zr-2 AND SOME EXPERIMENTAL ALLOYS.

do those with lower initial ductility. There is a greater change in ductility for initially more ductile materials than for those which were initially low in ductility. It should be pointed out that material which, when tested as coupons in irradiation tests, showed only 5 to 10 percent elongation to failure, has performed successfully as fuel cladding for a year to three years judging from the Dresden and Shippingport experience. At higher service temperatures (above about 360 C) in steam even less radiation damage is expected. (30, 31) Since the requirements for ductility for the alloy being designed here are primarily those determined by fabricability we have chosen the specification for ductility on the bases of our experiences in fabrication of some 130 different zirconium alloy compositions. We find that if the room temperature elongation to failure exceeds 20% and the reduction in area at room temperature is 35%, no problems with fabricability are experienced. Therefore, the specifications for ductility will be set in terms of room temperature fabricability at 20% elongation to failure and 35% reduction in area.

6. Strength

Since the design to which we are addressing ourselves here involves supported cladding, it is not necessary to make stringent requirements on strength. The alloys which could meet this requirement then would probably be expected to have strength levels about that of sponge zirconium itself. This is quite at the low end of the strength potential for zirconium alloys. Table VI gives an indication of the range of mechanical properties which can be developed in zirconium alloys. It should be noted in Table VI that there is almost an inverse relationship between the strength of an alloy and its corrosion resistance. It is very difficult to get steam corrosion resistance in high strength alloys, but at the lower

strength levels quite reasonable corrosion resistance can be obtained. This observation has also been made by Douglass⁽³²⁾ in studies on high strength zirconium alloys. Thus, in order to meet the rather stringent specification which we have placed on corrosion resistance it will be desirable to set the specification for strength in the alloy to be designed approximately at that of zirconium sponge. It should be noted that if an alloy is successfully designed to meet the corrosion requirements set here, then other methods and mechanisms of strengthening might be applied in subsequent studies to extend the applicability to those cases where higher strength is a more important requirement.

TABLE VI
EXPERIMENTAL HIGH STRENGTH ZIRCONIUM ALLOYS
500 C (932 F) Tensile Tests

	Alloy Content w/o		0.2% Yield Kpsi	UTS Kpsi	Elonga- tion %	Reduction in area %
	Alpha Stabilizers	Beta Stabilizers				
(A)	1.65 Al, 1.5 Sn		65	70	24	46
(A)	2.0 Al	1.0 Mo	59	61	35	66
(A)	1.5 Al, 0.6 Sn	0.8 Mo	52	60	43	53
(B)	0.5 Sn	1.0 Mo, 1.5 Nb	38	40	22	38
(C)	3.5 Sn	1.6 Mo	34	48	46	75
(C)(D)	2.0 Sn	1.5 Nb, 1.0 Cr	32	41	26	39
(C)		2.0 Nb, 1.0 Cr	23	29	41	86
(C)(E)		5.0 Nb	23	35	36	82
	(Zr-2) 0.55 Sn	0.3 Fe, Cr, Ni	19	23	64	66
	Zirconium Sponge		11	17	48	55

- (A) Disintegrate in short time in high temp. water; reportedly corrosion resistance in sodium.
- (B) Corrosion weight gain roughly 10 times that for Zr-2 in water and steam.
- (C) Corrosion weight gain roughly 3 times that for Zr-2 in 680 F water and 750 F steam (3000 hours).
- (D) 3000 hrs, 680 F static water; alloy $\Delta W = 80 \text{ mg/dm}^2$; alloy total hydrogen 76 ppm Zr-2 $\Delta W = 32 \text{ mg/dm}^2$; Zr-2 controls 51-72 ppm.
 3000 hrs, 750 F static steam; alloy $\Delta W = 320 \text{ mg/dm}^2$; alloy total hydrogen 324 ppm Zr-2 $\Delta W = 96 \text{ mg/dm}^2$; Zr-2 control 246 ppm.
- (E) 3000 hrs, 680 F static water; alloy total hydrogen 46 ppm
 Zr-2 controls 51-72 ppm.
 3000 hrs, 750 F static steam; alloy total hydrogen 173 ppm
 Zr-2 control 246 ppm.

Summary of Specifications

Specifications have been derived for the design of a zirconium base alloy for application in nuclear steam service for components which are thin sections such as fuel cladding and in which corrosion resistance to degradation of mechanical properties during service are the primary and critical requirements. the alloy to be designed would not require high strength as it would have application for supported or bonded fuel cladding or for co-extruded protective cladding on high strength alloys. Such an alloy would be useful for example, as cladding material for unbonded UO_2 fuel elements designed to rely on the fuel for support of the cladding. Fuel element designs of this kind are being developed for very thin stainless steel-clad UO_2 fuel. A summary of the specifications for the alloy design is given below:

1. The alloy shall have no alloying additions which would lead to an increased requirement for U-235 enrichment of more than .05% in a core having the general nuclear parameters of the Dresden Nuclear Power Station core.
2. The alloy shall have no alloying element and no problems with fabrication which would lead to an increase in cost of more than 5% over the cost of Zircaloy-2 tubing.
3. The alloy shall show less than 1500 ppm hydrogen in excess of the solubility limit in the alloy after a calculated service life of 3 years for a 25 mil tube corroding on one side. In lieu of this requirement the alloy would be acceptable if based on tensile and sheet impact test data after corrosion exposures -- it could be extrapolated that the alloy after 3 years of service would have a reduction in area of at least 8 ft-lbs at the service temperature or better.
4. The alloy shall have a corrosion rate when tested in out-of-pile steam tests of $1 \text{ mg/dm}^2/\text{day}$ or less as a post-transition corrosion rate.
5. The alloy shall have a room temperature ductility defined by

the values 20% elongation to failure and 35% reduction in area or better.

6. The alloy shall be as strong as sponge zirconium or stronger.

The temperature range of interest shall be from 300 C to 500C in steam at approximately 500 to 1500 psi pressure.

It will, of course, be necessary to study any alloy meeting these specifications for physical properties, including thermal conductivity and thermal expansion. It will be necessary to study the effect of radiation on mechanical properties and on the corrosion rate and hydriding rate of the alloy before its performance can be completely assessed for acceptability in any specific reactor design.

REFERENCES

1. O'Driscoll, W. G., C. Tyzack, and T. Raine, "Development of Zr Alloys Resistant to Gaseous Oxidation", Proceedings of the 2nd Geneva Conference, P/1450 UK, August 1958.
2. Wagner, R. K., H. E. Kline, D. I. Sinizer, "Zirconium Alloys for Cladding High Temperature Fuel Elements", Nuclear Metallurgy, Vol. VII, AIME, October 19, 1960
3. Lustman, B. and F. Kerze, The Metallurgy of Zirconium, McGraw-Hill Book Company, New York, 1955.
4. Chirigos, J. N., S. Kass, W. W. Kirk, and G. J. Salvaggio, "Development of Zircaloy-4", I.A.E.A. Symposium on Power Reactor Experiments, Vienna, October 1961.
5. Lustman, B., M. L. Bleiberg, E. S. Byron, J. N. Chirigos, J. G. Goodwin, and G. J. Salvaggio, "Zircaloy Cladding Performs Well in PWR", Nucleonics, Vol. 19, Jan. 1961, p. 58.
6. Perryman, E. C. W., "A Review of Zircaloy-2 and Zircaloy-4 Properties Relating to the Design Stress of CANDU Pressure Tubes", Atomic Energy of Canada Limited, Report CR-Met-937, June 1960.
7. Klepfer, H. H., "Utilization of Zircaloy-2 for Boiling Water Reactor Fuel Cladding", General Electric Co., Atomic Power Equipment Department, Report GEAP-3639, April 1961. Also appears in "Dispense del Corso di aggiornamento eu Combustibili e Materiali per impianti nucleari, II-Materiali per reattori", CNEN, ANDIN, Rome, February 1961.
8. Krenz, F. H.,

International Congress on Metallic Corrosion, London, April 1961.
9. Nelson, R. C. and D. S. Parker, "The Behavior of Zircaloy-2 Fuel Cladding in Boiling Water Reactor Tests", General Electric Co., Atomic Power Equipment Dept., Report in preparation.
10. Asher, R. C., B. Cox, J. K. Dawson, "Investigations Relating to the Use of Zircaloy-2 in Steam-Cooled Reactors", I.A.E.A. Symposium on Power Reactor Experiments, Vienna, October 1961.
11. Pemsler, J. P., "The Corrosion of Zirconium Alloys in 900 F Steam", Nuclear Metals Report, NMI-1208, August 1958.
12. Bieffer, G. J., L. M. Howe, A. Sawatsky, and F. H. Krenz, "Hydrogen Pick-up in Zirconium Alloys. A Review of Data up to June 1, 1959", Atomic Energy of Canada Limited, Report CR-Met-849, September 1959.

13. Cox, B., "Hydrogen Absorption by Zircaloy-2 and Some Other Alloys During Corrosion in Steam", J. Electrochem Soc., January 1962.
14. Klepfer, H. H., General Electric Co., Atomic Power Equipment Department, Report in preparation.
15. Brown, A. and D. Hardie, "The Effect of Dissolved Oxygen on the Terminal Solubility of Hydrogen in Alpha Zirconium", J. Nuclear Mat., 4, No. 1 (1961) 110-112.
16. Hardie, D., University of Durham, King's College, Private communication
17. Klepfer, H. H., "Zirconium Alloys for Steam Service - A Preliminary Study", General Electric Atomic Power Equipment Department, Report GEAP-3462, June 1960.
18. Klepfer, H. H., "Zirconium-Columbium Binary Alloys for Boiling Water Reactor Service. Part II - Corrosion Hydrogen Embrittlement", submitted for publication, March 1962.
19. Sawatsky, A., "The Diffusion and Solubility of Hydrogen in the Alpha Phase of Zircaloy-2", J. Nuclear Mat., 2, No. 1 (1960) 62-68.
20. Mudge, W. L., "Effect of Hydrogen on the Embrittlement of Zirconium and Zirconium-Tin Alloys", in Zirconium and Zirconium Alloys, ASM Cleveland, 1953.
21. Burton H. H., "Hydrogen Effects on Zircaloy-2 Tensile Properties", Hanford Atomic Power Operation, Report HW-61077, July 1959.
22. Klepfer, H. H. and C. N. Spalaris, "Mechanical Behavior of Cold-Worked Nuclear Grade Zircaloy-2 Tubing", Nuclear Metallurgy, Vol. VII, AIME, New York, October 1960.
23. Douglass, D. L., "Corrosion Problems in the Use of Zirconium and Columbium Alloys in Nuclear Reactors", Corrosion, Vol. 17, No. 1, December 1961, 105-110.
24. Yeniscavich, W., R. A. Wolfe, and R. M. Lieberman, "Hydrogen Absorption by Nickel-Enriched Zircaloy-2", J. Nuclear Mat., Vol. 3, 1959.
25. Rösler, U., "Studies on the Corrosion of Zirconium Alloys in Superheated Steam", Symposium Sur la Corrosion dans l'Industrie Nucleaire, Paris, October 19, 1961.
26. Klepfer, H. H., R. E. Blood, and D. W. Gaylor, "A Notched Sheet Impact Test for Studying Corrosion Hydrogen Embrittlement in Zirconium Alloys", in publication ASTM.

27. Pemsler, J. P., A. G. Tobin, and D. S. Kneppel, "Fundamental and Applied Research and Development in Metallurgy. Research on the Mechanism of Zirconium Alloy Corrosion in High Temperature Steam", Nuclear Metals Report NMI-1251, October 1961.
28. Douglass, D. L., General Electric Atomic Power Equipment Department, private communication.
29. Brutschy, F. J., General Electric Atomic Power Equipment Department, private communication.
30. Howe, L. M. and W. R. Thomas, "The Effect of Neutron Irradiation on the Tensile Properties of Zircaloy-2", Atomic Energy of Canada Limited, Report CR-Met-827, March 1959.
31. Howe, L. M., "The Annealing of Irradiation Damage in Zircaloy-2 and the Effect of High Temperature Irradiation on the Tensile Properties of Zircaloy-2", Atomic Energy of Canada Limited Report CR-Met-922, April 1960.
32. Douglass, D. L., "The Creep and Corrosion Behavior of Some High-Strength Zirconium Alloys", Nuclear Metallurgy, Vol. VII, AIME, 1960.

PART II SELECTION OF ALLOYING ADDITIONS

Introduction

In Part I of this study,⁽¹⁾ specifications were derived for the design of the zirconium-base alloy for application in nuclear steam service for components which are thin sections (such as fuel cladding) and in which corrosion resistance and resistance to degradation of mechanical properties during service are the primary and critical requirements. A summary of the specifications which were derived for the alloyed design is given below:

1. The alloy shall have no alloying additions which would lead to an increased requirement for U-235 enrichment of more than .05% in a core having the general nuclear parameters of the Dresden Nuclear Power Station core.
2. The alloy shall have no alloying elements and no problems with fabrication which would lead to an increase in cost of more than 5% over the cost of Zircaloy-2 tubing.
3. The alloy shall show less than 1500 ppm hydrogen in excess of the solubility limit in the alloy after a calculated service life of 3 years for a 25 mil tube corroding on one side. In lieu of this requirement, the alloy would be acceptable if -- based on tensile and sheet impact test data after corrosion exposures -- it could be extrapolated that the alloy after 3 years of service would have a reduction in area of at least 10% and a sheet - impact test energy-absorption value of at least 8 ft/.bs at the service temperature or better.
4. The alloy shall have a corrosion rate when tested in out-of-pile steam tests of $1 \text{ mg/dm}^2/\text{day}$ or less as a post-transition corrosion rate.
5. The alloy shall have a room temperature ductility defined by the values 20% elongation to failure and 35% reduction in area or better.
6. The alloy shall be as strong as sponge zirconium or stronger.

The temperature range of interest shall be from 300 C to 500 C in

steam and approximately 500 to 1500 psi pressure.

Each of the possible alloying elements in the periodic chart will be considered with respect to these specifications. Certain alloying elements will be eliminated on the basis of each specification and the known effect of these alloying elements on performance; other alloying elements will be discussed with regard to their known performance in promoting realization of the specifications. The elements which result from this analysis will be included in the experimental development program. A detailed analysis will be made of these elements to select composition limits based on available empirical data concerning hydrogen take-up and corrosion behavior. This final alloy field will then be re-checked against the specifications. Finally, the statistical choice of compositions within this alloy field which are to be melted and examined experimentally will be presented to complete Part II of this study.

Part III of this study will present the details of the experimental program to be carried out including procedures, anticipated form of results, and methods of data analyses. The results of the experimental program and final analyses will be reported in subsequent parts of this study.

Alloying Elements Eliminated or Chosen on the Basis of the Specifications

There are, of course, only a finite number of possible alloying elements for the zirconium alloy studies and considerable empirical data are available on the properties of these elements and their affects as alloying additions to zirconium. Some of these alloying elements which would be eliminated on the basis of one specification could also be eliminated on the basis of others. An example might be chlorine, which will be eliminated by considerations of its high vapor pressure, but would also be eliminated on the basis of its known adverse effect on corrosion. Also, some of the elements which will not be eliminated from consideration by any single specification will be eliminated by a combination of considerations. For example, palladium is not ruled out by its thermal-neutron capture cross-section or its cost or its effect on corrosion or its effect on

hydrogen embrittlement; but the combination of high thermal neutron cross-section, high cost and the promotion of high hydrogen pick-up and its promotion of poor corrosion performance when in combination with columbium additions will, in our judgement, remove it from inclusion in the experimental alloy field.

Certain elements from the residue of non-objectionable elements will be chosen for the study on the basis of positive performance. Certain others will be held for possible consideration as minor additions to the optimum composition which is found in the study. Some of these elements which would be held for possible consideration in later studies will be placed in that category primarily on the basis of limited or incomplete knowledge about the effect of these particular elements on hydrogen pick-up or on corrosion resistance, or because they are marginal in some other respects such as cost or neutron capture cross-section.

The elements in the periodic table will now be examined as possible alloy additions with respect to each of the specifications in turn.

1. Neutron Economy

Those elements with no stable isotopes and those with other undesirable nuclear properties such as those giving rise to fission reactions or fissionable reaction products under a neutron flux will be eliminated from consideration first. These elements which are shown on a schematic periodic table in Figure 1. Lithium, beryllium and boron are also somewhat undesirable as alloying elements due to the gases which would be generated in the alloy matrix under neutron bombardment.

For the remaining elements, we have calculated the effect on neutron economy when each element is used as a binary alloying addition to zirconium. The calculations were made using the nuclear parameters of a nuclear core like that of the Dresden Nuclear Power Station. These calculations are shown in Appendix A and the results are tabulated in Table I. As we have explained in Part I

of this study, we have chosen to limit alloying additions to those which, when added to the core in question, would give rise to a requirement for increased U-235 enrichment of no more than .05%. This percentage increase in enrichment is real. The impurity levels allowed in the accepted chemical specifications for Zircaloy-2 give rise to a requirement for an increase of U-235 enrichment on only 0.005%, for example. However, in practice U-235 enrichment control in nuclear fuel is to the nearest 0.1%. (In addition to the neutron economy limits on amount of alloy, there are also metallurgical and practical limits which will be discussed later, which could be more restrictive.)

For actual alloys having more than one alloying addition, of course, the limits permissible for any one alloying element will be reduced accordingly. Thus, tantalum additions, for example, would be permissible up to 1.4 w/o only if this were the only alloying element in the alloy. If palladium, for example, was also present and then the allowable amount of tantalum would be reduced. Therefore, we have included the calculation for weight percent limit for each element at 0.02% change in enrichment in Table I as a more useful guide for our studies.

It can be seen from the results of the calculations given in Table I that a number of elements are quite impractical as alloying additions in zirconium. Additions in the parts-per-million range can not be expected to be very effective in promoting good corrosion resistance or in reducing susceptibility to hydrogen embrittlement. The cost of control of composition in this range is prohibitive, particularly since little improvement in behavior is expected. Commercial experience with composition control does extend down to 500 ppm in the case of nickel in Zircaloy-2. Below that the only control is to eliminate certain undesirable impurities as far as possible. Therefore, those elements which have been calculated to have a limit of less than 500 ppm for an increase

in enrichment of .02% U-235 are eliminated from consideration in this study. These elements are also indicated in Figure 1. The values calculated in Table I will be taken as upper limits for this study. The upper limit will be studied, of course, only if there is some indication that alloy additions of this amount would promote the realization of the other specifications for the alloy. For example, hafnium additions as high as 1200 ppm would be of interest only if there is evidence that such additions greatly improve the corrosion resistance or resistance to corrosion hydrogen additions in zirconium.

2. Low Cost

The criterion here is that no alloying addition to zirconium would cause any increase in the cost of the resulting alloy over that now prevalent for Zircaloy-2 tubing, at least no more than 5% higher. A number of different factors need to be considered: the cost of the actual alloying element itself, the difficulty in control of its content in the alloy during melting by present commercial methods, and such matters as its toxicity, volatility and melting point.

With respect to the cost of the alloying addition itself, a calculation of the increase in cost for each of the several precious metal additions which might be considered has been made to see what weight percent limits would be set by 5% and 2% cost increase criteria. The results are given in Table II. We have included several elements which have already been eliminated on the basis of their thermal neutron capture cross-section simply to give perspective to the calculations made here. It should be noted that a great many of the common alloying elements are less expensive than the zirconium they replace in the alloy. On the other hand, many elements are limited to very low alloy additions by their cost. Due to the practical difficulty and cost of controlling composition below 500 ppm, seven more elements not

Eliminated Due To Undesirable Nuclear Properties Or Reactions

Eliminated Due To Adverse Effect On Neutron Economy

																H	He
Li	Be	B											C	N	O	F	Ne
Na	Mg	Al											Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No					

Figure 1. ALLOYING ELEMENTS ELIMINATED FROM THIS ZIRCONIUM ALLOY DESIGN BY NUCLEAR CONSIDERATIONS ALONE

TABLE I
WEIGHT PERCENT LIMITS FOR ALLOYING ELEMENTS FOR ZIRCONIUM ON
THE BASIS OF NEUTRON ECONOMY

Element	Wt % Limit for Increase in Enrichment of		$\sigma_a A_a$	A_a	σ
	$\Delta\% E=0.02$	$\Delta\% E=0.05$			
O	** 85.3	** 93.4	.011	5.70	.002
Bi	* 81.9	* 92.0	.014	.036	.033
C	** 73.4	** 87.4	.923	7.58	.003
F	A 59.5	* 78.6	.043	4.80	.099
Pb	* 46.6	* 68.7	.073	.43	.17
Be	** 38.7	** 61.2	.101	10.1	.010
He	* 28.5	* 49.9	.160	22.8	.007
Zr	F 27.2	F 47.0	.18	1.0	.18
Mg	22.0	40.5	.233	3.70	.063
Si	13.0	30.2	.423	3.25	.13
Ce	12.4	26.2	.45	.645	.70
Sn	12.2	25.6	.46	.769	.60
Rb	7.8	17.5	.749	1.07	.70
Al	7.5	17.0	.78	3.39	.23
Ba	7.4	16.6	.797	.664	1.2
Nb	6.1	14.1	.98	.983	1.0
Ca	6.1	14.1	.98	2.28	.43
Y	4.5	10.6	1.34	1.03	1.3
Sr	4.5	10.6	1.35	1.04	1.3
Ar	4.4	10.4	1.37	2.28	.6
S	4.4	10.2	1.39	2.84	.49
Tl	4.1	9.8	1.48	.45	3.3
Zn	4.0	9.4	1.54	1.4	1.1
Na	2.9	7.0	2.10	3.97	.53
Ru	2.7	6.3	2.26	.903	2.5
Mo	2.6	6.3	2.37	.95	2.5
Ge	2.2	5.2	2.90	1.26	2.3
Te	1.9	4.6	3.29	.715	4.6
Ga	1.7	4.0	3.80	1.31	2.9
Fe	1.5	3.9	4.10	1.64	2.5
Sb	1.5	3.7	4.12	.75	5.5
I	1.4	3.5	4.42	.70	6.3
Ne	1.4	> 3.4	< 4.52	4.52	< 1.0
K	1.4	3.3	4.66	2.33	2.0
Pt	1.3	3.3	4.67	.467	10.0
As	1.2	2.9	5.25	1.22	4.3
Cu	1.2	2.9	5.33	1.44	3.7
Cr	1.2	2.9	5.43	1.75	3.1
La	1.1	2.7	5.86	.66	8.9
P	1.1	2.6	5.88	.29	2.0

TABLE I (Continued)

Element	Wt % Limit for Increase in Enrichment of:		ϕ_{aAa}	Aa	ϕ
	$\Delta\%$ E-0.02	$\Delta\%$ E-0.05			
Pd	.93	2.3	6.88	.86	8.0
Pr	.88	2.2	7.12	.647	11.0
Ni	.88	2.2	7.13	1.55	4.6
Os	.88	2.2	7.18	.48	15.0
Br	.84	2.1	7.52	1.14	6.6
V	.71	1.8	8.78	1.79	4.9
W	.71	1.8	8.95	.50	18.
Ti	.56	1.4	11.0	1.84	6.0
Ta	.56	1.4	11.1	.50	22.
N	.52	1.3	12.4	6.5	1.9
Se	.44	1.1	15.1	1.16	13.
Yb	.32	.80	19.5	.53	37.
Cs	.30	.74	21.3	.69	31.
Mn	.29	.71	22.1	1.66	13.
Xe	.26	.64	24.3	.69	35.
Nb	.21	.56	30.3	.63	48.
H	.21	.53	30.4	90.8	.33
Kr	.20	.51	30.5	1.1	28.
Ho	.18	.45	35.4	.55	64.
Re	.15	.37	42.1	.49	86.
Tb	.14	.36	43.8	.97	45.
Au	.14	.35	45.4	.46	98.
Sc	.14	.34	46.7	2.03	23.
Ag	.12	.31	50.8	.85	60.
Hf	.12	.29	53.6	.51	105.
Lu	.11	.27	57.8	.52	111.
Co	.11	.23	57.3	1.55	37.
Tm	.09	.23	67.5	.54	125.
Cl	.08	.19	84.8	2.6	33.
Er	.063	.17	92.6	.54	170.
Rh	.048	.12	133.	.89	150.
In	.040	.10	151.	.79	190.
Hg	.040	.10	159.	.46	350.
Ir	.028	.072	218.	.47	460.
Dy	.010	.026	617.	.56	1100.
Li	.0068	.017	923.	13.1	71.
Cd	.0029	.0073	2175.	.81	3300.
Eu	.0024	.0062	2580.	.60	4300.
Sm	.0010	.0026	6070.	.61	10,000.
B	.0010	.0020	6365.	8.43	755.
Gd	.0002	.0007	22,040.	.58	38,000.

* Can be interpreted as allowing large increase in cladding wall thickness.

** Effect on moderator to fuel ratio is actually the most important consideration in these cases.

F Indicative of allowed change in wall thickness of base metal on a weight percent basis.

already eliminated on the basis of neutron economy are eliminated on the basis of the calculations shown in Table II. These elements are indicated in Figure 2. In addition ruthenium, rhenium, and holmium are dropped from consideration due to their limited availability. Those alloying elements which would be eliminated from this study because they require special alloying techniques not presently in commercial use are discussed next. Obviously the inert gases are eliminated as practical alloying elements. In addition, those alloying elements having vapor pressures of greater than 10 atmospheres at 2000 K, roughly the melting point of the zirconium alloy base, will be eliminated. This list includes the elements fluorine, chlorine, bromine, iodine, sulfur, phosphorous, arsenic, selenium, antimony, tellurium, zinc, sodium, magnesium, potassium, rubidium, and cesium (also shown in Figure 2). The elements F, Cl, Br, I, S, P, As, Zn, Na, Mg, K, Rb, and Cs would also be eliminated because of their adverse effects on the corrosion resistance of zirconium.

Another group of elements having high vapor pressures (above about 1 atmosphere at the melting point of zirconium and 100 times the vapor pressure of any element in Zircaloy-2) are noted. These elements include lead, bismuth, calcium, strontium, and barium; they will be considered further with respect to their effect on corrosion resistance.

One other alloying element, tungsten, would be severely limited in its usefulness because of its high melting point. A number of investigators have recorded difficulty in getting homogeneous alloys of tungsten with zirconium.

There are also two elements whose usefulness is limited by their toxicity. These elements are beryllium and thallium.

A large number of elements have been eliminated due to considerations of cost and difficulty in processing by present commercial

Eliminated Due To High Cost

Eliminated Due To Low Availability And High Cost

Eliminated Due To Vapor Pressure (>10 atmos. at 2000°K)

*** Also Have Very Adverse Effect On Corrosion Resistance**

55

Figure 2. ALLOYING ELEMENTS ELIMINATED FROM THIS ZIRCONIUM ALLOY DESIGN BY COST CONSIDERATIONS

WEIGHT PERCENT LIMITS FOR ALLOYING ELEMENTS FOR ZIRCONIUMON THE BASIS OF COSTTABLE II

Element	Wt % Limit for Increase Cost of		Approximate Cost Dollars per pound Minus Cost of Zr Sponger Replaced (\$6/lb)		Annual Production
	2%	5%			
Sc	.003	.008	18,160	(1)	Very limited
Lu	.012	.939	5,448	(1)	Very limited
Eu	.016	.040	3,859	(1)	
Tm	.016	.040	3,859	(1)	
Ir	.024	.060	2,474	(2)	300 lbs
Os	.028	.070	2,034	(2)	100 lbs
Rh	.032	.080	1,814	(2)	
Tb	.032	.080	1,816	(1)	
Ga	.044	.11	1,354	(2)	200 lbs
Pt	.044	.11	1,349	(2)	
Ru	.052	.13	1,159	(2)	300 lbs
Re	.064	.16	904	(2)	200 lbs
Au	.12	.29	504	(2)	
Si	.14	.35	324	(2)	
Yb	.15	.38	400	(1)	
Pd	.17	.44	344	(2)	
Ge	.18	.45	334	(2)	
B	.19	.48	312	(2)	
Ho	.24	.59	254	(1)	Very limited
Er	.24	.59	254	(1)	
Gd	.25	.62	244	(1)	
Dy	.25	.62	244	(1)	
Y	.28	.70	214	(1)	
Sm	.35	.89	169	(1)	
Pr	.37	.91	164	(1)	
Nd	.42	1.0	144	(1)	
La	.58	1.4	104	(1)	
Ce	.58	1.4	104	(1)	
Hf	.64	1.6	94	(1)	
Be	.64	1.6	94	(2)	
Ta	1.7	4.3	35	(2)	
V	1.8	4.4	34	(2)	
In	2.2	5.6	27	(2)	
Sr	3.3	8.3	18	(2)	
Nb	4.3	11.	14	(1)	
Tl	6.7	17.	9	(2)	
W	6.7	17.	9	(2)	
Cr	6.7	17.	9	(1)	
Ba	8.0	19.	8	(2)	
Ag	10.0	25.	6	(2)	
Li	15.	38.	4	(2)	
Cg	30.	75.	2	(2)	
Mo	60.		1	(2)	

TABLE II (Continued)

The following elements are less expensive than the zirconium they replace by alloying. (2)

<u>Element</u>	<u>Cost</u>
Ti	6.00
Se	3.50
Co	2.60
Hg	2.50
Bi	2.55
Cd	2.00
Te	1.50
Sn	.85
As	.70
Ni	.60
Mn	.32
Cu	.30
Sb	.29
Mg	.27
Al	.20
Na	.17
Pb	.14
Ar	.10
Fe	.04

- (1) Data compiled by the author from recent quotations for metal of the purity required for alloy with zirconium.
- (2) Data from Reference 2, p. 642.

methods, and several others whose usefulness is limited by these considerations have been noted.

3. Low Susceptibility to Hydrogen Embrittlement

The requirement that alloying elements for this alloy design not lead to increased susceptibility to hydrogen embrittlement obviously eliminates hydrogen as an alloying element.

No complete study of the effect of alloying elements on percent corrosion hydrogen take-up has been made. Considerable data can be found for the effect of nickel, iron, chromium, tin, antimony, columbium, and vanadium. Some data are available for the effect of palladium, platinum, molybdenum, tantalum, and titanium. Limited data for copper, oxygen, arsenic, bismuth, and tellurium have also been taken. Unfortunately the data available for some of these elements, eg, Mo and Ti, are for compositions outside the range of interest in this study. Some of the elements for which there are data have already been eliminated from consideration in this study for reasons relating to neutron economy and cost (eg. As, Pt and Te).

The adverse effect of nickel on corrosion hydrogen pick-up in zirconium alloys was revealed by the studies of Yeniscavich and co-workers.⁽³⁾ Hydrogen pick-up increases with increasing nickel reaching 40-80% at about 0.1 w/o Ni, 80-9-% at 0.5 w/o Ni, and essential 100% at 1.0 w/o Ni according to several investigators.^(4,5) In spite of the fact that nickel also promotes good corrosion resistance in steam, its promotion of very high pick-up percentages eliminates it from primary consideration in the present study.

Our studies of the effect of palladium additions on hydrogen take-up indicated rapidly increasing hydrogen take-up with increasing palladium content - quantitatively equal in effect to that reported for nickel (100% pick-up at 1 w/o).⁽⁶⁾

This fact along with the moderately adverse effects of palladium on neutron economy and cost are taken to eliminate palladium from primary consideration in this study.

Our data for molybdenum⁽⁶⁾ combined with those of Cox, Davies, and Dent⁽⁷⁾ indicate that hydrogen pick-up decreases with increasing molybdenum. However, at levels below 1 w/o Mo, which will be required to maintain good ductility,⁽⁸⁾ our very limited data indicate that molybdenum promotes a high percentage hydrogen take-up. Thus, molybdenum will not be given primary consideration in this alloy study.

Berry, Vaughn and White,⁽⁴⁾ Cox, Davies and Dent,⁽⁷⁾ and the author⁽⁹⁾ have studied hydrogen take-up in Zr-Cr alloys. At 360 C in water, Berry et al found 15-34% pick-up for 0.5-1.30 w/o Cr alloys. We found about 10% for 0.2-3.0 w/o Cr alloys at 360 C. In steam, Cox et al have only one point for a 48 day exposure at 400 C for a Zr - 2 w/o Cr - 1 w/o Sn alloy; the hydrogen pick-up was 25%. Our data in steam indicate no strong composition dependence, but show considerable scatter. The post-transition pick-up percentage ranges from 30 to 80%. The higher figure is most probable (see Figure 1 Part I of this study. Ref. (1)). (The most corrosion resistant alloy, Zr - 1.0 w/o Cr, showed a very low hydriding rate of 400 C in steam and moderate rate at 482 C).

Berry, Vaughn and White⁽⁴⁾ found that 0.3-0.5 w/o Sn added to sponge zirconium had no effect on hydrogen take-up in 360 C water. Kass studied iron-tin ternaries and found that their hydrogen take-up was determined largely by the iron content. At 360 C in water, 0.5 w/o Sn additions were better than 0 or 1.0 w/o additions to iron binaries. At 400 C in steam increasing tin in the ternaries promoted a moderate decrease in hydrogen take-up.⁽¹⁰⁾ Our data for Zr-Nb-Sn-Mo and Zr-Cr-Sn-Mo indicate that pick-up was not determined by tin content.⁽⁶⁾ Thus, tin additions are

apparently rather innocuous with respect to corrosion hydrogen in zirconium alloys.

The effect of iron on the percentage hydrogen take-up in zirconium alloys has received considerable experimental attention. Berry, Vaughn and White⁽⁴⁾ studied 0.16, 0.24, 0.50, and 1.07 w/o Fe alloys at 360 C in water and found a minimum of 24% pick-up for the 0.24 w/o alloy. Kass studied compositions from 0.29-1.54 w/o iron at 360 C in water (197 days) and 400 C in steam (112 days) and found that hydrogen pick-up increased from 22-50% in the low weight percent alloys to 50 to 100% in the 1.54 w/o alloy.⁽¹⁰⁾ Our data⁽⁹⁾ for 360 C, 400 C, and 482 C also show increasing pick-up with increasing iron above 0.2 w/o Fe. In steam at 400 C and 482 C we found the post transition pick-up percentage for the 0.2 w/o alloy to be about 35%. Alloys of 1.5, 2.0, and 3.0 w/o iron show corrosion hydrogen pick-up percentages of essentially 100 %. (Since the iron binaries show good corrosion resistance in steam, the 0.2 w/o iron alloy generally showed the lowest hydriding rate of any of the twenty binary alloys included in our studies).

Berry, Vaughn and White's results⁽⁴⁾ (and ours⁽⁹⁾) for the effect of antimony additions to zirconium on hydrogen take-up at 360 C show that antimony promotes very low (perhaps less than 10%) take-up. When present in higher order alloys such as Zircaloy-2, however, its effect is evidently over-shadowed by the effect of other elements present.^(4,10) In steam at 400 C and above, our data⁽⁹⁾ and those of Cox, Davies and Dent⁽⁷⁾ indicate that the post-transition percentage hydrogen take-up is on the order of 30%. (However, the corrosion resistance of Zr-Sb alloys in steam is very poor so that the over-all hydriding rate in steam is prohibitive.⁽⁹⁾)

Columbium additions to sponge zirconium lead to a low percentage hydrogen take-up. Fisch⁽¹¹⁾ reports about 10% pick-up in Zr-Nb-Sn

alloys at 360 C and 400 C. Dalgaard^(12,13) gives values from 8 to 30% at 400 C for 2.5 w/o Nb alloys with and without tin additions in various heat treatments. Anderko and co-workers⁽¹⁵⁾ report 13-34% pick-up at 400 C in steam for alloys ranging in composition from 0.4-40 w/o Nb. Rösler's⁽¹⁴⁾ data show 30-50% post-transition take-up in 1.0 and 2.5 w/o Nb alloy tested in steam at 500 C. Our recent studies indicate pick-up percentages between 12 and 25% at both 400 and 482 C in steam, depending on heat treatment and film thickness. (We find that hydriding rates are very low at 360 C and 400 C for alloys containing less than 0.2 w/o Nb. For 2.8 and 4.2 w/o Nb alloys comparatively low rates were observed at 482 C. Mechanical property tests have revealed a low susceptibility to corrosion hydrogen embrittlement in alpha-annealed Zr-Nb alloys.⁽¹⁶⁾)

Only two alloys containing tantalum additions within the composition range of interest in this study have been analyzed for hydrogen take-up. Alloys containing 0.1 w/o and 1.0 w/o Ta picked up between 10 and 40% of the corrosion hydrogen in steam tests at 400 and 482 C.⁽⁹⁾ These data are not extensive enough, however, to recommend tantalum as an alloying addition of primary interest. Both our studies⁽⁹⁾ and the earlier study of Cox, Davies and Dent⁽⁷⁾ indicate that vanadium additions to zirconium promotes a low percentage (less than 20%) of corrosion hydrogen take-up by the metal. (We find, however, that the corrosion resistance of Zr-V alloys in steam at 400 C and 482 C is quite poor. The overall effect is a moderately high total hydrogen take-up in these alloys.⁽⁹⁾)

Copper is reported by Cox, Davies and Dent to promote moderately low hydrogen take-up,⁽⁷⁾ but their steam data are not conclusive. Kass and Kirk report that increasing oxygen in the narrow range of practical interest promoted somewhat lower hydrogen take-up in Zircaloy-4.⁽¹⁷⁾ All that is known about the effect of bismuth is

that up to 0.5 w/o added to Zircaloy-2 does not lower the hydrogen take-up and that in the range 0.1 to 0.2 w/o Bi the corrosion resistance of the Zircaloy-2 was impaired.⁽⁴⁾

Only two elements are known to perhaps promote increased solubility for hydrogen in the underlying metal in corroding zirconium alloys, and these are oxygen and columbium. Oxygen is not a very effective element in increasing hydrogen content solubility for the range of usable oxygen additions -- according to the data of Brown and Hardie.⁽¹⁸⁾ We have found that columbium additions to zirconium apparently increases the solubility for hydrogen.⁽¹⁶⁾ This has been supported by the studies of Hardie,⁽¹⁹⁾ who found the solubility of hydrogen in a zirconium-columbium binary alloy to be increased at 300 C. This observation in the case of columbium, then, leaves columbium as one of the alloying elements of definite interest in this alloy design study since it is apparently unique in giving significant increases in solubility for hydrogen and, therefore, would be recommended for decreasing susceptibility to hydrogen embrittlement. Considering the effect of various alloying elements on the percentage of hydrogen that passes through the corrosion film, we would also find that columbium would be recommended in steam.

On the basis of the preceding review we would choose for emphasis in this alloy study: columbium because of its effect on increasing solubility and its low percentage of hydrogen pick-up; iron and chromium because of the reasonable observed percentages pick-up and the low weight gain of hydrogen versus time in certain Zr-Fe and Zr-Cr alloys. Considerations of susceptibility to hydrogen embrittlement have eliminated hydrogen, nickel, palladium, and molybdenum from primary consideration in the present alloy study.

Corrosion

Referring now to Figure 3, it can be seen that a large number of

the alloying elements have been eliminated on the basis of the considerations of neutron economy, cost, and susceptibility to hydrogen embrittlement. For the remaining elements there is a large body of empirical experience which indicates that many of these elements are detrimental to the corrosion resistance of zirconium alloys. On the other hand, there is also evidence that a number of these alloy additions lead to very good corrosion resistance in steam.

Examples of alloying elements which lead to good corrosion resistance in steam are iron and chromium, which have been studied by Pemsler^(20,21) and by others, and also copper, based on the Canadian work reported by Thomas⁽²²⁾ and the work at the Argonne National Laboratory reported by Greenberg.⁽²³⁾ We have studied columbium as a binary addition to zirconium and find that these alloys have better steam corrosion resistance than that of Zircaloy-2.⁽²⁴⁾ These four elements are recommended on the basis of their effect on steam corrosion resistance.

The remaining elements in Figure 3 will be discussed with respect to their effect on the steam corrosion resistance of zirconium. Beryllium additions to zirconium are limited to rather low weight percentages due to the sharp decrease in melting point (from ~1860 C at 0 w/o Be to 930 C at about .4 w/o Be. Kass⁽²⁵⁾ reports in the minutes of the Zirconium Corrosion Committee that 1.0 w/o Be is definitely detrimental to the corrosion resistance of Zr. Neither beneficial nor harmful effects were noted for additions up to 0.62 w/o in Zircaloy-2. Considering also the undesirable nuclear reaction in Be under neutron bombardment, its toxicity and its high cost, beryllium will not be given primary emphasis in the present alloy study.

Considering the other elements of groups II and III of the periodic table, it has been found in a number of studies, including Thomas' early studies reported in Lustman and Kerze's

Figure 3. Alloying Elements Eliminated From This Zirconium Alloy Design On The Basis Of Corrosion Resistance

book^(25,26) and our own experience,⁽⁶⁾ that calcium, aluminum, yttrium, lanthanum, and the rare earths cerium, neodymium and erbium all have a very detrimental effect on the corrosion resistance of zirconium. Therefore, all group II and group III elements and the rare earths will be eliminated from consideration on the basis of their adverse effect on corrosion resistance.

Moving on to the transition elements, we can see that titanium is detrimental to corrosion resistance in zirconium up to about 4 w/o.^(25,26) Since titanium additions would be limited to less than 4% by nuclear economy considerations, titanium is eliminated from interest as an alloying element in this study. Hafnium is even more limited in usefulness by its high neutron cross-section; and, Thomas⁽²⁶⁾ reports no beneficial effect on corrosion which would justify including it in this study.

The data available for the effect of vanadium on steam corrosion resistance is conflicting. In summarizing the early work, Thomas lists Zr-V alloys as "inferior to pure zirconium" in corrosion resistance.⁽²⁶⁾ More recent studies at the Armour Research Institute indicate that a 1.0 w/o vanadium alloy addition gives rise to good corrosion resistance at 400 and 482 C in steam.⁽²⁷⁾ This has not been confirmed by our experiments at longer times as the data in Figure 4 show. Vanadium additions do lead to low values for post-transition hydrogen pick-up, however, and will be set aside as additions of secondary interest for this study.

We have not studied tantalum additions in great detail although we have made some binary alloys with 0.1 and 1.0 w/o Ta which performed equivalent to, but no better than, comparable columbium containing alloys.⁽⁶⁾ Weinstein⁽²⁷⁾ gives data indicating fair performance for a 0.25 w/o Ta alloy. Russian investigators studied crystal bar base Zr-Nb-Ta alloys,⁽²⁹⁾ which performed very well. Since tantalum is more restricted than columbium by

neutron economy and cost and shows no better indications of promoting low hydrogen pick-up than does columbium, tantalum will also be set aside as an addition of secondary interest.

Early studies indicated that tungsten additions were deleterious to the corrosion resistance of zirconium, at least at low temperatures.⁽²⁵⁾ Weinstein has recently studied 0.25 and 1.0 w/o W alloys which showed poor performance in steam.⁽²⁷⁾ These facts, combined with the restrictions set by neutron economy and melting difficulties, force the elimination of tungsten as an alloying addition of interest.

There is no evidence that manganese additions to zirconium are anything but harmful with respect to corrosion resistance.^(25,26) Since manganese is also restricted by considerations of neutron economy no further attention will be given to this element as a possible alloying element.

Cobalt additions to zirconium promote good corrosion resistance^(25,27) but not more so than iron which has a much lower thermal-neutron capture cross-section. As a secondary addition to an optimum alloy cobalt with its low neutron economy would be limited to additions in the range below 500 ppm, which, as we have discussed, is of little practical interest. Cobalt is therefore eliminated from this study.

Silver and gold additions will also be eliminated from consideration. Gold is deleterious to the corrosion resistance of zirconium,⁽³⁰⁾ as is silver.^(27,30) The cost and neutron economy limitations on these elements further restrict them from even secondary interest.

There are no data known for the effect of thallium on the corrosion resistance of zirconium. The extreme toxicity of this element and its unknown effect on corrosion will be taken to exclude it as an alloying possibility.

The interstitial alloying elements carbon and nitrogen, as pointed out in Thomas' review in 1955, of the corrosion of zirconium,⁽²⁶⁾ have long been known to be detrimental to the corrosion resistance of zirconium alloys. Oxygen was also found in the early studies to be detrimental above certain levels although at the level of oxygen which we will be studying (levels below 3000 ppm), oxygen is rather innocuous in its effect on corrosion resistance.⁽²⁵⁾ Oxygen is, however, not to be considered as an alloying element in these studies, but rather an impurity which will be held at a practical and controlled value while other compositional changes are made.

Additions of silicon to zirconium were first reported to be deleterious in their effect on corrosion resistance.^(25,26) The recent studies at Metallgesellschaft⁽³¹⁾ show a beneficial effect for 0.05%-0.3% Si in sponge zirconium at 400 C in steam. However, studies at the Armour Research Foundation show that silicon is not one of the better alloying additions for steam corrosion resistance.⁽²⁷⁾ The case of silicon additions (and incidentally tellurium⁽²⁷⁾ and antimony⁽²⁸⁾ additions) is an interesting one. The beneficial effects appear to be limited to very narrow compositional ranges -- which apparently vary with impurity content in the zirconium. It is as if a delicate electron to atom ratio balance were being disturbed by impurities (of low valence). These three elements, Si, Te, and Sb will, therefore, be set aside for secondary interest in the alloy design.

The metalloid element germanium, on the other hand, has never been shown to be anything but deleterious;^(27,30) it will not be included in this study.

The case of tin and also antimony is rather special in that these elements are known to give increased tolerance for nitrogen impurity, which is very desirable; however, both tin and antimony

Figure 4. CORROSION WEIGHT GAINS FOR Zr-V BINARY ALLOYS IN STEAM (400°C)

are very deleterious to steam corrosion resistance.^(20,26,27,28) Of the two elements, tin is the worst in this regard.⁽²⁸⁾ The addition of these elements in zirconium alloys is made to either increase strength or to improve low temperature corrosion resistance. Since strength is not a primary consideration in this study, additions for strengthening are not required. The low temperature corrosion improvement is not too different for the two elements, with tin perhaps the best in this regard.⁽²⁸⁾ The real advantage is an increased tolerance for nitrogen. We find nitrogen contamination a problem only for service below 600 F in water, however. At 680 F and at higher temperatures we have found that up to 200 ppm nitrogen can be tolerated in tin-free and antimony-free alloys.^(24,28) Nitrogen control and specifications must be kept as tight as those for Zircaloy-2, however, and perhaps tightened closer to actual commercial capability (from 80 ppm maximum to 50 or 60 ppm maximum for example.) With nitrogen in control there appears to be no over-riding requirements for tin or antimony additions. Therefore, tin (and antimony) will be of only secondary interest in the present study.

Finally, the alloying elements lead and bismuth are eliminated from this study. These elements both have moderately high vapor pressures, as has already been mentioned, and in the summary of the early zirconium alloy work, Thomas reports that lead has adverse effects on the corrosion resistance of zirconium.⁽²⁶⁾

A Zr-0.25 w/o Bi alloy has been tested in steam at 400 C; the alloy showed a very high rate of corrosion.⁽²⁷⁾

At this point, it would be very advantageous if there were available a fruitful theory about the corrosion mechanism in zirconium. It would be very desirable to be able to state what the combined effects of two different alloying elements would be on corrosion resistance based on first principles. That is, we are eliminating elements which, by themselves, as binary additions to zirconium

are known to lead to poor corrosion resistance. However, it is not clear on any theoretical grounds that combinations of two or more elements which by themselves are deleterious would necessarily be deleterious, but might in fact, be helpful. There has been one experimental investigation of a possible theoretical approach but the results were somewhat disappointing. Misch⁽³²⁾ considered a valence approach to the problem where additions which have lower valence than zirconium are balanced with higher valence alloying additions in order to promote good corrosion resistance. He found, however, many cases in which this approach alone did not hold. In fact, only a few cases were reported in which it did hold, one was a combination of scandium (low valence) and molybdenum (high valence). This combination would not be of practical interest because of the high thermal neutron capture cross-section and cost of scandium. Thus, we are forced to make the conservative assumption here that the effect of the alloying elements which are deleterious by themselves, will be to lead to poor corrosion resistance when in combination with other elements.

In summary then, considerations of corrosion resistance have eliminated a number of elements as shown in Figure 3 and have recommended the use of columbium, iron, and chromium and copper as alloying additions to promote high temperature steam corrosion resistance.

5 & 6. Ductility and Strength

It is required in the specifications that the zirconium alloy to be designed shall have a good room temperature ductility to promote fabricability; quantitatively, that the elongation be at least 20% to failure, that the reduction area be 35%. However, it is not required that the alloys developed be high strength, rather only that they be intermediate in strength between sponge zirconium. Therefore, there will be no additional consideration

of the elements on the basis of strength requirements alone.

With respect to ductility and fabricability there are a number of elements which are known to promote a sluggish transformation of beta zirconium to alpha during fabrication giving coherent-precipitate strengthening and very low ductility. These elements include tungsten which we have already eliminated on the basis of other considerations, but also include molybdenum, tantalum, vanadium, and columbium which are of primary or secondary interest. However, it has been found for additions of tantalum⁽²⁹⁾ and columbium⁽²⁴⁾ below about 5 w/o that these additions should not give rise to difficulty in fabricability. Above this, a transition phase which is extremely embrittling is found in these alloys⁽³³⁾ and limits metallurgically the additions of columbium which are practical for the alloy being specified here.

Another mechanism of strengthening zirconium alloys is particle strengthening due to the presence of intermetallic compounds. Only one element of primary or secondary interest, however, would promote real brittle behavior in the range of composition of interest and that element is beryllium. This fact will be taken to limit the composition of interest to less than 0.15 w/o beryllium.

A third mechanism of strengthening in zirconium alloys, and one which if carried to its ultimate, leads to low ductility, is solid solution strengthening. Of the alloying elements of interest for consideration, only oxygen has extensive solid solubility in zirconium and it does, in fact, at levels above 3000 ppm lead to decreases in ductility in zirconium alloys; therefore our intention in this study is to control the oxygen content to a level of 2000 ppm or below.

We must consider the effect of the total alloying addition on the fabricability in setting the limits as we will do in sub-

sequent sections on the amount of alloying addition to be added. It has been our experience that for zirconium binary sponge-base alloys (containing moderate levels of oxygen) that alloys containing large amounts of either those elements leading to coherent precipitates or, particularly, alpha-stabilizing elements such as tin and aluminum that the limit for excellent fabricability is at about 2 w/o total alloy addition. However, for the beta-stabilizing elements in the ranges of composition which remain in consideration for this alloy design (including columbium) we have found that total alloy weight percentages of 4 w/o to 5 w/o give rise to alloys which can be readily fabricated and which should meet the criteria which we are using here in determining the acceptability in terms of ductility.

Thus far all the elements in the periodic table, except columbium, chromium, iron, and copper have been eliminated from primary interest. In addition, there are a number of elements which might be considered later as minor alloy additions to the optimum composition for alloys having the additions we have just named. These elements which might be studied in a subsequent experiments include oxygen, beryllium, tin, molybdenum, tantalum, vanadium, antimony, silicon, tellurium, palladium, and nickel within the weight percent limitations set forth in Table III. The limits assigned in Table III have been assigned on the basis of neutron economy, hydrogen embrittlement, cost, effect on corrosion resistance, and effect on strength and ductility. It will be seen that these are all quite minor alloying additions. It is conceivable that additional information will become available concurrent with our study which will either aid in the choice of these elements or eliminate some of them from further consideration, and we mention them here merely to indicate that there may be narrow composition regions in which these alloy additions could be useful. We can not make a firm conclusion because of the lack of a quantitative and fruitful theory of corrosion mechanism for zirconium alloys which would indicate the effect to be expected for combinations of various elements.

We will discuss in subsequent paragraphs what is known empirically about combinations of those elements which remain of primary interest for this alloy design.

Alloy Field

In the preceding section, after considering the specifications for this particular alloy design study, the known effects of various alloying elements on the properties of zirconium which are related in this specification were considered. We have chosen four alloying elements to be included in the alloy field for this study. They are columbium, chromium, iron, and copper. It remains to consider the compositional limits which will be placed on each of these alloying elements in order to describe the alloy field in which this study will be made, and then to re-check this alloy field against the specifications for the design.

A. Composition Limits

The fabricability of Zr-Nb alloys limits the alloy additions to something less than 4 w/o. This limit will be taken for the study at hand. We have found that alloys low in columbium content (essentially single-phase alloys) perform very well in corrosion tests in terms of total hydrogen take-up at low steam temperatures, that is 360 C and 400 C. These low alloying additions alone do not give rise to alloys which perform well at 482 C in steam. However, with increasing columbium content the performance in steam becomes much better and the hydrogen solubility apparently increases with increasing columbium content so that the whole range of columbium additions up to 4 w/o is of interest.

The chromium limits were selected on the basis of total hydrogen weight gain for Zr-Cr binaries after long-term corrosion tests. Our data in this respect show that there is a minimum of hydrogen weight gain at about 0.5 w/o to 1.5 w/o chromium.⁽⁹⁾ This range, then, will be taken for this study. Our data also show that 1.0 w/o chromium alloys performed better with respect to corrosion

TABLE IIIALLOYING ELEMENTS OF SECONDARY INTEREST

<u>Element</u>	<u>Probable Working Limit (w/o)</u>	<u>Maximum Limit</u>	<u>Basis of Limit</u>	<u>Basis of Interest</u>
O	0.20	0.30	Ductility, corrosion	Strength
Be	0.10	0.15	Ductility	Strength (Corrosion)
Sn	0.50	0.75	Corrosion	Strength (N ₂)
Mo	0.25	1.00	Ductility	Strength (Corrosion)
Ta	0.15	0.56	Neutron economy	H ₂ (corrosion)
V	0.20	0.71	Neutron economy	H ₂ (corrosion)
Sb	0.50	0.50	Corrosion	H ₂ (take-up)
Si	0.10	0.30	Control of composition	Corrosion
Te	0.25	0.25	(vapor pressure)	Corrosion
Pd	0.05	0.10	H ₂ take-up	Corrosion
Ni	0.05	0.10	H ₂ take-up	Corrosion

resistance than Zircaloy-2 at all temperatures of test. At higher weight percentages of chromium, about 3 w/o, we find very good performance at 482 C in steam as far as corrosion resistance is concerned, but this high an alloy percentage in addition to a high columbium addition would give rise to difficulties in fabricability. There is apparently no adverse effect of combinations of columbium and chromium as alloying additions to zirconium on its corrosion resistance. A zirconium-0.5 w/o columbium-1.0 w/o chromium alloy was among the best ternary alloys which we have studied.⁽²⁹⁾ We have also studied zirconium-columbium-tin-chromium alloys and zirconium-columbium-antimony-chromium alloys, these alloys have all performed reasonably well in steam; therefore, there is no evidence that the addition of chromium and columbium together to zirconium alloys will lead to deleterious effects.

The range of composition of interest with iron again is determined by a sharp minimum in the total hydrogen weight gain after long corrosion exposures of certain compositions. Based on the work of Berry and co-workers⁽⁴⁾ and on our data⁽⁹⁾ (which agree quite well), there is a very sharp minimum in hydrogen weight gain at about 0.25 w/o iron. We will limit this study, then, to compositions including iron from 0.15 to 0.35 w/o. At higher weight percentage of iron both the percentage hydrogen going through a corrosion film and the total hydrogen weight gain after long exposures increase markedly. The combinations of iron with the other two elements we have thus far discussed have been studied in some detail with respect to effect on corrosion behavior. Pemsler⁽²¹⁾ has, of course, studied chromium and iron combinations in great detail, they are included in the Zircalloys, and there is no indication of anything but very good corrosion performance with this combination. We have also studied ternary zirconium alloys containing both columbium and iron.⁽²⁸⁾ Our alloys which contained about 1 w/o iron and either 0.5 or 2 w/o Nb performed fairly well.

It should also be noted that the Russian alloys which are considered to be the optimum in their development for steam, the Ozhennite alloys, contain both columbium and iron and perform very well.⁽²⁹⁾

The selection of a composition limit for copper is determined by a number of factors. First of all, the thermal neutron capture cross-section for copper is quite high so that amounts in addition to those we have set for columbium, chromium, and iron must be quite low to maintain a reasonable macroscopic cross-section in the resulting alloys. Furthermore, the additions must be quite limited due to the restriction on total alloy content for purposes of fabricability. The range of alloy compositions which have been the most widely studied are from 0.5 to 1.5 w/o copper. It is in this range that we know the most about the effect of copper as an alloying element and we will accept that as the composition range of interest in this study. With regard to combinations of copper with the other alloying elements being considered, the columbium-copper ternary combination is reported to be good, the chromium-copper combination is unknown, unfortunately, but the iron-copper combination is reported on the basis of preliminary studies to give rise to very good corrosion performance in steam.⁽²³⁾

In summary, the alloy field for the design of a zirconium alloy for steam service will include the field bounded by 0 to 4 w/o columbium, 0.006 w/o (in sponge), or 0.5-1.5 w/o chromium, 0.03 w/o (in sponge) or 0.15-0.35 w/o iron, and zero or 0.5-1.5 w/o copper.

Rechecking the Specifications

In Table IV we have listed the macroscopic capture cross-section for the alloys having high, low, and middle levels of additives within our alloy field and compared these with zirconium and with stainless steel. We have also examined these high, low and middle compositions with respect to our Dresden core calculations and those results are

listed also in Table IV. It should be pointed out that the macroscopic capture cross-section of the actual resulting alloys cannot be calculated precisely without the densities of the resulting alloys so that the values given in Table IV are estimated until the densities of the alloys can be determined. It will be seen, however, that the alloy field contains compositions which will not meet the specification for neutron economy. It is desirable, however, in order to accurately determine the response coefficients R_n to have some data outside the acceptable field.

It will be noted that alloying additions in the alloy field selected will require no special melting methods which are not now in commercial practice. The addition of 4 w/o columbium to the alloy, which is the maximum of the only alloying element more expensive than zirconium, would add less than approximately 2% of the present cost of the Zircaloy-2 tubing. Thus, it would appear that there should be no difficulty within the alloy field of meeting the specifications on cost.

In reviewing the effects of the alloying additions in the alloy field for their effect on corrosion-hydrogen embrittlement it is noted that the columbium addition is one of the most helpful additions because of its low percentage hydrogen passing through the corrosion film and because of its effect to increase the solubility in hydrogen. Chromium and iron as we have seen, lead to low values of total hydrogen weight gain at least for 3000 hour exposures in steam. It is necessary to hold iron to low levels in order to avoid susceptibility to corrosion hydrogen embrittlement, but this has been done within the alloy field selected. The best information for copper is that it should not lead to high susceptibility corrosion hydrogen embrittlement. Therefore, it appears that the specification for low susceptibility to corrosion hydrogen embrittlement can be met and that there is good chance that it can be met in the alloy field selected.

TABLE IV

NEUTRON ECONOMY PARAMETERS - ALLOY FIELD

<u>Alloy</u>	<u>Σ (Macroscopic Cross Section)*</u>	<u>Calc $\Delta\%$ E U-235**</u>
Zr	.0077	
Low:		
0.25 w/o Nb		
0.09 w/o Fe	.0100	.019
0.5 w/o Cr		
0.5 w/o Cu		
Middle:		
2.0 w/o Nb		
0.25 w/o Fe	.0132	.043
1.0 w/o Cr		
1.0 w/o Cu		
High:		
4.0 w/o Nb	.0163	.066
0.35 w/o Fe		
1.5 w/o Cr		
1.5 w/o Cu		
Stainless steel	.26	

$$* \quad \Sigma = \frac{N_A \rho}{100} \left[\left(\frac{W_1 \sigma_1}{B_1} \right) + \left(\frac{W_2 \sigma_2}{B_2} \right) + \dots + \frac{W_n \sigma_n}{B_n} \right] \quad \text{Assume } \rho = 6.5 \text{ g/cc.}$$

$$** \quad \Delta\% \text{ E-U-235} = 0.314 \left[W_1 A_1 \sigma_1 + W_2 A_2 \sigma_2 + \dots + W_n A_n \sigma_n \right] \quad \text{See Appendix A}$$

Where: W_n is weight % element n. Summation includes Zr for Σ only

ρ is density in g/cc

N_A is Avogadro's number $6.03 \times 10^{23} \text{ moles}^{-1}$

B is atomic weight element

A is atomic weight additive/atomic weight Zr

σ is microscopic cross-section in barns

In reviewing our alloy field with respect to the corrosion specification of $1 \text{ mg/dm}^2/\text{day}$ for long time post-transition corrosion rate, it is noted that none of the alloying additions by themselves have been demonstrated to meet this specification at the highest temperatures of interest. Iron and chromium are the best of the four additions over the entire temperature range of interest, copper is considered deleterious at low temperatures, at least in water, but has shown fairly good performance in high temperature steam. Columbium, at low columbium additions is excellent at low temperatures but not good in 482 C steam. On the other hand, high columbium additions are better than Zircaloy-2 by far at high temperatures but have corrosion rates about twice that of Zircaloy-2 at low temperatures. This addition is in the right direction for the design we need for this application. It will be necessary to control nitrogen because in the alloy field we do not have any of the alloying additions which are known to be good for offsetting the adverse effect of nitrogen at low temperatures. A limit of 60 ppm nitrogen will be set and any material which does not fall below this specification will be rejected from the test.

It might be noted that the lowest corrosion rates reported thus far for zirconium alloys in high temperature steam, about $1.0\text{-}1.5 \text{ mg/dm}^2/\text{day}$, were those reported by Greenberg⁽²³⁾ and by Pemsler⁽²¹⁾ for Zr-Fe-Ni alloys at 538 C. It is also interesting to note that all of the other zirconium alloys which are successful with respect to their steam corrosion resistance contain elements which we have in our alloy field. For example, Zircaloy-3 and the other Zircaloys contain iron and chromium. The poor performance of Zircaloys in steam is believed due to tin, which we have not included. The Russian Ozhennite alloys⁽²⁹⁾ contain tin also, but contain iron and columbium (and nickel which is detrimental with respect to hydrogen embrittlement). Also among the best zirconium alloys which Pemsler reported were alloys which contained combinations of iron and chromium. The best alloys

which we have tested are zirconium-iron binaries and zirconium-columbium-chromium ternaries. The best zirconium alloys for gas-cooled reactors (which also look good in steam) contain copper-molybdenum additions. There is also preliminary evidence that copper-columbium and iron-copper additions give alloys which perform very well in steam. Thus, there is apparently good evidence that if the corrosion specification can be met, it should be met by a composition in the alloy field which we are studying.

In the case of the ductility specification, we have seen that there are no particular problems with fabricability as we have taken this into account in setting the composition limits. For an alloy containing the highest alloying additions of all elements in the alloy field at once there might be some difficulty with fabricability, but there is a good probability that the alloy meeting the other specifications will also be fabricable. It is necessary to address ourselves to the problem of heat treatment in getting good ductility and getting good corrosion resistance and this will be taken up in a subsequent paragraph.

The alloy field selected has alloying additions which should, based on our past experience, give, for the low side of total alloying additions, strengths like sponge zirconium. At the high end a few of the possible combinations might give strengths exceeding that of Zircaloy-2, but probably by not more than 20%. Thus, it is almost certain that the rather non-restrictive specification on strength will be met.

C. Heat Treatment

It is necessary to set a heat treatment for the alloys which are to be studied which will lead to a metallurgically stable structure so that the response to the environment in terms of strength and corrosion resistance is not changed during test and so that the ultimate response to radiation does not give rise to changes in

properties due to the effect of radiation on metastable phases. It is also desirable that a fine microstructure be produced by heat treatment in order to be consistent with the existing theories about what microstructure promotes good corrosion resistance in zirconium alloys.

Before considering what this heat treatment should be, it would be worthwhile to review the phase diagrams for the four alloy systems being considered. These are presented in Figures 5, 6, 7, and 8. It will be seen that the lowest temperature limit for the stability of the alpha phase is about 610 C in the case of the zirconium-columbium system. This then would limit the upper temperature for the final heat treatment in order to assure homogeneous structure. It will be noted that intermetallic compounds will be expected in all of the alloys within the alloy field because of the low solubility of iron, chromium, and copper in zirconium. Another phase which may be present would be a solid solution of about 18% zirconium in columbium which is the phase in equilibrium with alpha zirconium below 610 C in the zirconium-columbium system. We have recently reported that the presence of this phase is desirable in decreasing the susceptibility of the corrosion-hydrogen embrittlement as it is postulated that this phase has a very high solubility for hydrogen. Various investigators have pointed out the importance of having a fine, uniform distribution of the intermetallic compounds to promote good corrosion resistance. Thus, it would be desirable to quench from the beta region where all these elements would be in solid solution in order to maintain homogeneity and then to anneal in the alpha region in order to precipitate the alloying elements to give a metallurgically stable microstructure. Recent studies on zirconium-columbium binaries indicate that a long-time anneal on the order of 24 hours at temperatures around 565 C to 595 C lead to the optimum corrosion resistance in the zirconium-columbium binaries. (15,24)

Figure 5. ZIRCONIUM-COLUMBIUM SYSTEM (After Lundin)

Figure 6. ZIRCONIUM-CHROMIUM SYSTEM (After Hayes et al & Domagala et al)

Figure 7. ZIRCONIUM-IRON SYSTEM (After Hayes et al)

Figure 8. ZIRCONIUM-COPPER SYSTEM (After Lundin et al)

This treatment would not be inconsistent with promoting good corrosion resistance in the iron-chromium systems according to the study by Pemsler.⁽²⁰⁾ The effects of heat treatment in the case of zirconium-copper alloy, it must be admitted, are relatively unknown, but the Zr-Cu alloys, judging from the phase diagrams, should not respond so differently to heat treatment than Zr-Fe or Zr-Cr alloys. Therefore, the heat treatment selected for this study consists first of a homogenization treatment at 927 C-982 C for 4 to 12 hours in the beta region, followed by quenching to room temperature before the final cold rolling in fabrication. After the final cold rolling fabrication step the alloys will then be held for 24 hours at 565 C for a stabilization and precipitation anneal.

Alloys for Statistical Analysis of Performance

In an attempt to locate the optimum composition in the alloy field selected and to determine the functional relationship between the chemical and mechanical properties and the amounts of the alloying elements we have chosen to use an experimental design which is outlined below.

The alloys to be melted are given in Table V. It will be noted that this design has both combinations moderately low and moderately high values of each element (nos. 1-8) and also has a mid-point of the alloy field represented (no. 31). There are alloys at the maximum for each element with the other elements at their mid-points (nos. 9-12). There are also alloys representing the absence or nominal value of each of the alloying additions (nos. 13-16), the absence or nominal value of two in combination (nos. 17-22), and there are alloys from each binary system included (nos. 23-26). There is also a group of alloys added to include very low contents of columbium (at the mid-point of Fe and at mid-point and nominal values of Cr and Cu, (nos. 27-30). There

are 31 alloys to be melted in the first run in the investigation of the alloys for steam service.

It should be pointed out that it may be necessary to have additional runs after this initial run. The first possibility is to take a more restricted alloy field within this alloy field in order to find an optimum composition in the event that there is a very sharp optimum in the field. Another possibility is that it would be desirable to make alloy additions from elements of secondary interest which we have listed in Table III to the optimum composition if there is evidence at that time that any of these elements should give real improvement beyond that for the optimum alloy in the alloy field that we have selected here as the primary area of investigation for this study.

It may appear that some of the 31 alloys in run #1 may not have desirable properties. However, the purpose of run #1 is to establish the relationships between the amounts of the additives and the properties of interest. It is also important to establish what levels of the additives are not satisfactory. Hence, data from all 31 alloys will be useful.

The data obtained from the design in Table V will be used to estimate the unknown parameters, b 's, in the following model:

$$\begin{aligned} R = & b_0 + b_1 (\text{Nb}) + b_2 (\text{Cr}) + b_3 (\text{Fe}) + b_4 (\text{Cu}) \\ & + b_5 (\text{Nb})^2 + b_6 (\text{Cr})^2 + b_7 (\text{Fe})^2 + b_8 (\text{Cu})^2 \\ & + b_9 (\text{Nb}) (\text{Cr}) + b_{10} (\text{Nb}) (\text{Fe}) + b_{11} (\text{Nb}) (\text{Cu}) \\ & + b_{12} (\text{Cr}) (\text{Fe}) + b_{13} (\text{Cr}) (\text{Cu}) + b_{14} (\text{Fe}) (\text{Cu}) \end{aligned}$$

where R is the response (corrosion rate, post-corrosion tensile reduction in area, sheet-impact energy absorption, hydrogen concentration, elongation to failure, area reduction, or strength) and Nb, Cr, Fe, and Cu are the w/o of these four additives. The model in eq. (1) is the linear and quadratic terms of a Taylor's

TABLE VRUN #1 ALLOYS

Alloy	Nb w/o	Cr w/o	Fe w/o	Cu w/o	Total Additives w/o
1	.50	.50	.14	.50	1.64
2	.50	.50	.30	1.00	2.30
3	.50	1.00	.14	1.00	2.64
4	.50	1.00	.30	.50	2.30
5	2.00	.50	.14	1.00	3.64
6	2.00	.50	.30	.50	3.30
7	2.00	1.00	.14	.50	3.64
8	2.00	1.00	.30	1.00	4.30
9	4.00	.75	.22	.75	5.72
10	1.00	1.50	.22	.75	3.47
11	1.00	.75	.35	.75	2.85
12	1.00	.75	.22	1.50	3.47
13	0	.75	.22	.75	1.72
14	1.00	.006	.22	.75	1.98
15	1.00	.75	.03	.75	2.53
16	1.00	.75	.22	0	1.97
17	0	.006	.22	.75	.98
18	0	.75	.03	.75	1.53
19	0	.75	.22	0	.97
20	1.00	.006	.03	.75	1.79
21	1.00	.006	.22	0	1.23
22	1.00	.75	.03	0	1.84
23	1.00	.006	.03	0	1.04
24	0	.75	.03	0	.78
25	0	.006	.22	0	.23
26	0	.006	.03	.75	.79
27	.25	.006	.22	0	.48
28	.25	.75	.22	0	1.22
29	.25	.006	.22	.75	1.23
30	.25	.75	.22	.75	1.97
31	1.00	.75	.22	.75	2.72

series of the function relating Nb, Cr, Fe, Cu, to R. Estimates of the b's are readily obtained by a least squares analysis employing an electronic computer.

It is desired to find the alloy in the field $0 \leq \text{Nb} \leq 4$, $.006 \leq \text{Cr} \leq 1.5$, $.03 \leq \text{Fe} \leq .35$, and $0 \leq \text{Cu} \leq 1.5$ w/o, that minimizes the corrosion rate subject to the conditions:

- (1) Strength $\leq$ sponge zirconium,
- (2) Room temperature elongation to failure $\leq 20\%$,
- (3) Room temperature reduction in area $\leq 35\%$,
- (4) (a) hydrogen concentration minus the solubility limit ≤ 1500 ppm (after 3 yrs. for 25 mil tube), or
 (b) tensile reduction in area $\leq 10\%$ (after 3 yrs.) and sheet-impact energy absorption at service temperature ≤ 8 ft-lbs (after 3 yrs.).

In addition the alloy must not lead to an increase in fabrication costs of more than 5% over Zircaloy-2 tubing and less than a .05% increase in U-235 enrichment for a Dresden type core.

From the data, the b's in eq. (1) will be determined for corrosion rate, R_1 , tensile reduction in area, R_2 , sheet-impact energy absorption, R_3 , hydrogen concentration, R_4 , elongation to failure, R_5 , area reduction, R_6 , and strength, R_7 . A search for the minimum value for R_1 will be made by an electronic computer for those combinations of additives that yield $R_2 \leq 10\%$ and $R_3 \leq 8$ ft-lbs or $(R_4 - \text{sol. limit}) \leq 1500$ ppm, $R_5 \leq 20\%$, $R_6 \leq 35\%$, and $R_7 \leq$ sponge zirconium strength. It may be desirable to test a second series of alloys centered about the optimum alloy from run 1 in order to improve the alloy and determine its sensitivity to slight changes in the amounts of the additives. At this time, it might also be desirable to add other elements (Table III) to the optimum alloy from run 1.

By a systematic choice of test alloys it will be possible to

relate the various properties of interest to the amounts of Nb, Cr, Fe, and Cu added. From these mathematical relationships, the combinations of values of Nb, Cr, Fe, and Cu which satisfy certain specifications can be determined by an electronic computer. Then, the alloy giving the minimum corrosion rate meeting these specifications can be estimated from the mathematical relationship between corrosion rate and Nb, Cr, Fe, and Cu as determined from the data.

Summary

We have considered those alloying elements and their composition limits which might be added to zirconium in order to develop a zirconium alloy which would meet the specifications which have been derived in Part I of this study. The alloy field which we have selected includes the region bounded by 0-4.0 w/o columbium, 0.5-1.5 w/o chromium, 0.15-0.35 w/o iron, and 0.5-1.5 w/o copper. Alloys in this alloy field will be given a special heat treatment including homogenization in the beta region, followed by beta quenching and a subsequent post-fabrication anneal in the alpha region to give a fine equilibrium structure. Nitrogen content will be controlled at less than 60 ppm nitrogen. With these limitations, it is our judgement that the optimum composition for meeting the specifications we have derived will be found in this alloy field and that there is a good probability that within this field the composition can be found which will meet the specifications. The alloys to be melted for actual experimental examination have been chosen by statistical experimental design in order to facilitate finding the optimum composition in the alloy field; these compositions are given in Table V. Elements chosen for secondary interest as possible addition to the optimum alloy in the alloy field are given in Table III.

APPENDIX A TO PART II

The Effect on Neutron Economy of Various Alloy Additions to Zirconium Cladding in a Nuclear Reactor Core Having the Parameters of the Dresden Nuclear Power Station

Calculations and Assumptions

The effect of alloying additions to the cladding on the reactivity k and on the required U-235 enrichment can be calculated by first examining the thermal utilization factor f for the reactor. The thermal utilization factor is the probability that a neutron will be captured by a uranium atom in the reactor and is given by

$$f = \frac{N_U \sigma_U}{N_U \sigma_U + \sum_i N_i \sigma_i} \quad (1)$$

where N_U is the number of uranium atoms

σ_U is the microscopic thermal capture cross-section of uranium

$N_i \sigma_i$ is the product of the number of atoms of a given element and the microscopic cross-section of the element and the summation is over all atoms in the reactor, excepting those of uranium

Differentiating both sides of equation (1) with respect to small additions to the reactor, one obtains

$$\frac{\Delta f}{f} = - \frac{\Delta \left[\sum_i N_i \sigma_i \right]}{N_U \sigma_U - \sum_i N_i \sigma_i} = - \frac{N_a \sigma_a}{N_U \sigma_U + \sum_i N_i \sigma_i} \quad (2)$$

where the subscript a refers to the additive and the other symbols have the significance assigned above.

Since the additives in this case are assumed to be made essentially uniformly to the cladding, any geometrical effects would be negligible and

$$\frac{\Delta f}{f} = \frac{\Delta k}{k} \quad (3)$$

to a good approximation.

Furthermore, for small changes in k it can be assumed that the change in percent enrichment $\Delta\% E$ required by the addition is proportional to $\Delta k/k$. Thus

$$\Delta\% E = \alpha \frac{N_a \sigma_a}{N_U \sigma_U + N_i \sigma_i} \quad (4)$$

These calculations assume that the alloying addition is to the cladding and that all the resulting material stays in the reactor. In fact, of course, the subject cladding would be replaced by the proposed alloy cladding. Thus some base metal is replaced by additive in practice. The effect of this approximation on the validity of the estimates depends on the density of the actual alloys produced. If the alloy density is less than that of the cladding base material, then the estimate will be conservative. This follows if the replacement is made with the same wall thickness since less non-fissionable material will be required in the reactor. If the alloy density turns out to be greater than that of the base material, then the estimate could be low. Since most of the additives are made in small quantity, the density changes will not be large. Barring an unusual density increase due to a crystal structure change, the estimate in this last case should still be within at least 0.05% of the necessary enrichment. With these qualifications in mind, the effect on neutron economy of additions to zirconium base cladding can thus be estimated quite closely using the Dresden design parameters.

For zirconium base cladding and Dresden conditions Equation (4) becomes

$$\begin{aligned} \Delta\% E &= + \alpha \left[\frac{N_a \sigma_a}{N_U \sigma_U + N_O \sigma_O + N_H \sigma_H + N_{Zr} \sigma_{Zr}} \right] \\ &= + \alpha \left[\frac{N_{Zr} \sigma_a}{\frac{N_U}{N_{Zr}} \sigma_U + \frac{2N_U}{N_{Zr}} + \frac{1/2N_H}{N_{Zr}} \sigma_O + \frac{N_H}{N_{Zr}} \sigma_H + \sigma_{Zr}} \right] \end{aligned} \quad (5)$$

where: $\frac{N_a}{N_{Zr}} = f = \left(\frac{\text{wt. add}}{\text{Wt. Zr}} \right) \left(\frac{\text{At. wt. Zr}}{\text{At. wt. add}} \right)$

$$\frac{N_U}{N_{Zr}} = \frac{\text{g-atoms U}}{\text{g-atoms Zr}} = \left(\frac{115,000 \text{ lbs U}}{43,000 \text{ lbs Zr}} \right) \left(\frac{91.22}{238} \right) = 1.01$$

$$\frac{N_H}{N_{Zr}} = \frac{N_H}{N_U} \frac{N_U}{N_{Zr}} = \left(\frac{\text{Vol. H}_2\text{O}}{\text{Vol. UO}_2} \right) \left(\frac{\rho \text{ UO}_2}{\rho \text{ H}_2\text{O}} \right) \frac{2}{1} \left(\frac{\text{M.W. UO}_2}{\text{M.W. H}_2\text{O}} \right) (1.01) = (2.17) (10.2) (2) \left(\frac{270}{18} \right) (1.01) = 6.69$$

The design data were taken from the Dresden Preliminary Hazards Report, GEAP-1044, and cross-sections from the G.E. Chart of the Nuclides, e.g.,

$$\sigma_{Zr} = 0.18, \sigma_H = 0.33, \sigma_O = 0.022, \text{ and } \sigma_{U_{1.5\% \text{ Enriched}}} = 13.24$$

and thus

$$\begin{aligned} \%E &= \alpha \left(\frac{f_a \sigma_a}{13.55 + .01 + 2.19 + 0.18} \right) \\ &= \alpha \frac{f_a \sigma_a}{15.93} \end{aligned} \quad (6)$$

Note that the capture cross-section of zirconium ($\sigma = 0.18$) rather than that of Zircaloy-2 ($\sigma \approx 0.20$) was used.

Discussions with Weil and Russell indicate that $\alpha = 5$ is conservative figure for the Dresden design so that

$$\Delta \%E = \left(\frac{5}{15.93} \right) f_a \sigma_a = 0.314 f_a \sigma_a \quad (7)$$

for additions to zirconium base material in the Dresden core.

Since the effect of additions on a weight percent basis is most useful in alloy work, it is noted that

$$f_a = \left(\frac{\text{wt. fraction add.}}{1 - \text{wt. fraction add.}} \right) \left(\frac{\text{At. wt. Zr.}}{\text{Ar. wt. add.}} \right)$$

Let $\frac{\text{wt. fraction add.}}{1 - \text{wt. fraction add.}} = F_a$ the weight ratio

and $\frac{\text{At. wt. Zr.}}{\text{At. wt. add.}} = A_a$ the Atomic weight ratio

So that

$$\Delta \%E = 0.314 F_a A_a \sigma_a \quad (8)$$

for additions to zirconium.

Conversion from F_a to weight percent can be made employing the simple relation

$$\text{wt.pct.add.} = \frac{F_a}{1 + F_a} (100).$$

For weight percents below about 5 it can be safely assumed that

$$\text{wt.pct.add.} \approx F_a (100).$$

Results

It is assumed here that development of alloys with truly improved high temperature corrosion resistance could justify changes in enrichment on the order of 0.05%. Using equation (8) in the Appendix and the enrichment change just mentioned, the maximum weight percent alloy additions permissible for various elements added to zirconium were calculated. The results are given in Table I of the main body of the report. Most of the elements included are of immediate or speculative interest, but some are included mainly for comparative purposes. It is important to recall that the calculations assume that all alloying elements are added to the reactor.

Discussion

The results in Table I for additions of element for which the $\sigma_a A_a$ value is less than that for the base metal, indicated by an asterisk, can be interpreted as indicative of a large permissible increase in cladding wall thickness using such alloys. Obviously, replacement of equal wall thickness would allow a decrease in enrichment since the resulting material would be of lower macroscopic cross-section than the base metal.

The metallurgical feasibility of alloys of the compositions indicated has been disregarded for the purposes of the calculations.

It should also be noted that there are other nuclear considerations not taken into account here. The addition of light elements might cause a re-evaluation of the moderator to fuel ratio. Furthermore, the capture cross-section of materials in the reactor in addition to affecting the thermal utilization also affects the conversion ratio.

The equations developed and the calculations performed serve the purpose of distinguishing composition ranges of "good" nuclear economy from those of "bad" nuclear economy, but particular compositions developed and tested should be submitted to the physicists for final evaluation of the nuclear design modification required by their use.

REFERENCES

1. Klepfer, H. H., "The Design of A Zirconium Base Alloy for a Specific Nuclear Application. Part I. Specifications", March 6, 1962.
2. Hampel, C. A., Rare Metals Handbook, Reinholdt Publishing Corp., London, (1961).
3. Yeniscavich, W., R. A. Wolfe, and R. M. Lieberman, "Hydrogen Absorption by Nickel Enriched Zircaloy-2", J. Nuclear Materials, 1, (1959) 271.
4. Berry, W. E., D. A. Vaughn, and E. L. White, "Hydrogen Pick-up During Aqueous Corrosion of Zirconium Alloys", Corrosion, 17 (1961) 109t.
5. Krenz, F. H., "The Steam and Water Corrosion of Zirconium Alloys", International Congress on Metallic Corrosion (December 1960).
6. Klepfer, H. H., "Zirconium Alloys for Steam Service - A Preliminary Study", GEAP-3462 (June 1960).
7. Cox, B., M. J. Davies, and A. D. Dent, "The Oxidation and Corrosion of Zirconium and Its Alloys. Part X. Hydrogen Absorption During Oxidation in Steam and Aqueous Solution", AERE-M621 (April 1960).
8. "A Study of the Mechanisms of Heat Treatment of Zr-Base Alloys". (Summary Report No. 3) COO-211, July 1955 to June 1956.
9. Klepfer, H. H., "Hydrogen Take-up During Water and Steam Corrosion of Alloys in Five Binary Zirconium Alloy Systems", in preparation for publication (1962).
10. Kass, S., "Hydrogen Pick-up in Various Zirconium Alloys During Corrosion Exposure in High Temperature Water and Steam", J. Electrochem. Soc., 107, (1960) 594.
11. Fisch, H. A., "Hydrogen Absorption by Zr-2 Atom % Sn - 2 Atom % Nb Alloy During Corrosion", KAPL-2149 (January 1961).
12. Dalgaard, S. B., "The Corrosion Resistance of Zr-Nb and Zr-Nb-Sn Alloys in High Temperature Water and Steam", CR-Met 911 (1960).
13. Dalgaard, S. B., "The Corrosion Resistance of Zr-Nb and Zr-Nb-Sn Alloys in High Temperature Water and Steam. Part II", CRGM-1030 (1961).
14. Rösler, N., "Studies on the Corrosion Resistance of Zirconium Alloys in Superheated Steam", Symposium Sur la Corrosion dans l'Industrie Nucleaire, Paris (October 1961).

15. Anderko, K. W. Jung-Konig, H. Richter, H. W. Schleicher and U. Zwicker, "Investigation of Zirconium with Niobium and/or Silicon in View of Their Use as Sheathing Material in Water-Cooled Nuclear Reactors", 3rd Quarterly Report by Metallgesellschaft, (January 1961).
16. Klepfer, H. H., "Zirconium-Columbium Binary Alloys for Boiling Water Reactor Use. Part II. Corrosion Hydrogen Embrittlement", submitted for publication (1962).
17. Kass, S. and W. W. Kirk, "Effect of Iron and Oxygen Variations on the Corrosion and Hydrogen Uptake Behavior of Zircaloy-4", in WAPD-ZH-24 (1960).
18. Brown, A. and D. Hardie, "The Effect of Dissolved Oxygen on the Terminal Solubility of Hydrogen in Alpha Zirconium", J. Nuclear Materials, 4, (1961) 110.
19. Hardie, D., Kings College, Durham. Private communication.
20. Pemsler, J. P., "The Corrosion of Zirconium Alloys in 900 F Steam", NMI-1208 (1958).
21. Pemsler, J. P., "Corrosion of Zirconium Alloys in 900 F and 1000 F Steam", NMI-1235 (1960).
22. Thomas, W. R., "Zirconium Alloys for Water-Cooled Power Reactors", IAEA Symposium on Fuel Element Fabrication with Special Emphasis on Cladding Materials, Vienna (May 1960).
23. Greenberg, S., "Zirconium Alloys for Use in Superheated Steam", J. Nuclear Materials, 4 (1961) 334.
24. Klepfer, H. H., "Zirconium-Columbium Binary Alloys for Boiling Water Reactor Use. Part I. Corrosion Resistance", submitted for publication (1962).
25. Kass, S., "Report of October 1954 Meeting of the Zirconium Alloy Committee", WAPD-MM-713 (1954).
26. Thomas, D. E., Metallurgy of Zirconium (Lustman and Kerze), McGraw-Hill, New York (1955).
27. Weinstein, D., "Improved Zirconium Alloys", ARF 2198-18, Quarterly Report April 1961 - June 1961, (1961).
28. Klepfer, H. H., unpublished work.

29. Arbartsumyan et al, "Mechanical Properties and Corrosion Resistance of Zirconium and Its Alloys in Water, Steam, and Gases at Elevated Temperatures", 2nd Geneva Conf., 15/P/2044 USSR (1958).
30. Boyd, W. K., D. J. Maykuth, R. S. Peoples, and R. I. Jaffee, "Compositional Factors Affecting Corrosion Resistance of Zirconium in High Temperature Water and Steam", BMI-1056 (1955).
31. Anderko, W., W. Jung-Konig, H. Richter, H. W. Schleicher and U. Zwicker, "Investigation on Alloys of Zirconium with Niobium and/or Silicon in View of Their Use as Sheathing Material in Water-Cooled Nuclear Reactors", 2nd Quarterly Report by Metallgesellschaft (October 1960).
32. Misch, R. D. and C. Van Drunen, "Corrosion Studies of Ternary Zirconium Alloys in High Temperature Water and Steam", ANL-6370, (July 1961).
33. Cometto, D. J., G. L. Honze, F. A. Hultgren, and R. F. Heheman, "Transformation Kinetics of Zirconium-Niobium Alloys", Department of Metallurgical Engineering, Case Institute of Technology, Interim Report No. 3, USAEC (July 31, 1960).

II. (TASK A) CORROSION MECHANISM

Introduction

The mechanism of zirconium alloy corrosion in high temperature water and steam has been extensively studied during the last decade, but our understanding of the corrosion process is still not adequate to design alloys based on a knowledge of the fundamental properties of the alloys and oxide films. Task A of this program was designed to provide additional understanding to the overall corrosion process, and although the efforts will be insufficient to enable a complete understanding to be obtained, it is anticipated that this work will answer some of the more pressing questions.

These questions are summarized as follows.

- (a) What is the nature of the protective oxide film on a corroding zirconium alloy with respect to chemical composition, permeability to oxygen and hydrogen, mechanical properties, and electrical properties -- and how are these properties changed as the alloy content of the sample changes from alloy to alloy or from surface depletion due to preferential oxidation of a given constituent?
- (b) What is the role of the intermetallic compounds present as second phases in the metal substrate with respect to hydrogen pick-up in the alloy during corrosion?
- (c) What is the correlation between oxide film properties (and intermetallic compounds) with steam corrosion behavior?

The program required to answer these questions has been subdivided into five subtasks:

- (1) Determination of oxide film compositions.
- (2) Relationship between film composition and corrosion behavior.
- (3) Partitioning of alloying elements and oxygen between substrate and film.
- (4) Hydrogen overvoltage and electrochemical properties of zirconium intermetallic compounds.
- (5) Diffusion of oxygen and hydrogen through pure and doped

zirconium dioxide and mechanical properties of the oxides.

The status of each subtask will be discussed separately after a brief technical description when applicable of why the work is being performed.

1. Oxide Film Compositions - D.L. Douglass, M.E. Urata

Program Description

The fact that oxide films of the same structure, monoclinic, form on both corrosion resistant and non resistant zirconium alloys indicates that some factor other than the type of oxide is controlling the rate of corrosion. Further, the time for transition to linear reaction kinetics does not depend upon oxide crystal structure and varies considerably from alloy to alloy. It would thus appear that the composition of the oxide varies from alloy to alloy or during the corrosion process of a given alloy and that the corrosion rate is dependent upon the defect structure of the oxide which is in turn determined by the presence of foreign cations.

It is not unreasonable to expect a preferential oxidation of an alloy constituent which is in solution on the basis of large differences in the free energy of formation between zirconium dioxide and the respective oxides of the solutes. Thus, unequal rates of oxidation will result in a depletion or concentration of alloying elements at the metal surface depending upon whether the rates are greater or less than that of zirconium, respectively. A buildup or depletion of foreign cations will occur in the oxide. Subsequent corrosion will then be affected in two ways. First, the changes in surface composition will cause the alloy to have a different resistance to corrosion and thereby change the oxidation rate. Second, the variation of oxide film composition will alter the defect structure and oxygen diffusion rates in the film which will also result in changes in the oxidation rate. It is therefore imperative to determine the oxide film compositions and to determine what, if any, changes take place at various stages of the corrosion process.

Experimental Program

Techniques have been developed to strip corrosion films from sheet samples which had been corroded for extensive periods (100-115 days) on an earlier program. Portions of one side of the film are mechanically removed to expose substrate metal. The samples are then exposed to 4M bromine solutions in ethyl acetate containing 0.3 gm MgO at 75 C in a reflux flask for one hour. The metal selectively reacts with the bromine to form soluble metal bromides, leaving the ZrO_2 film unreacted. The absence of reaction of the oxide was confirmed by a prolonged series of exposures of bulk zirconia in the solution. No attack was evident by gravimetric techniques. Additional proof tests of single component oxides, CuO, Fe_2O_3 , and NiO were also performed and revealed no reaction. The corresponding metals were all attacked and completely converted to soluble bromides in one hour.

A series of Zr-Nb-Sn, Zr-Sn-Cr, Zr-Nb-Cr, and Zircaloy-2 alloys have been subjected to film stripping. Wet chemical analyses and X-ray fluorescence are currently being performed and will be available for the second quarterly report. It is planned to perform similar tests on binary, solid solution alloys which will be corroded for various times at two different temperatures. The final data analysis will then be made in terms of the oxidation of discrete second phase particles and of solid solutions.

2. Relation Between Film Composition and Corrosion-D.L. Douglass

This portion of the program will be performed upon completion of subtask 1, Oxide Film Composition, and therefore will be deferred to a future report.

3. Partitioning of Alloy Elements-D. L. Douglass

Program Description

The chemical analyses of oxide films described in subtask 1 will give the overall composition of the films but will not provide a detailed

description of the microscopic changes. It is of considerable interest to learn the extent of depletion or enrichment of solutes at the oxide-metal interface and to ascertain the distribution of cations within the oxide itself. There is some evidence⁽¹⁾ that the alloying additions in Zircaloy-2 are highly localized in the corrosion films. It is desirable to study the tendency of the localized areas of alloying additions to dissolve into the oxide film to give a homogeneous solution and to observe changes in defect structure upon solution of the foreign cations.

Experimental Program

It is planned to perform microprobe analyses on alloys which contain both additions in solid solution and as second phase particles. The microprobe traverses will be made in the oxide film as well as in the metal substrate adjacent to the oxide-metal interface. The specific compositions of the alloys have not been selected yet but will be chosen upon completion of subtask 1. If heterogeneous areas are detected in the oxide film, additional runs will be made for various exposure times during corrosion to determine the extent of homogenization.

4. Hydrogen Overvoltage--S. J. Armijo, F. A. Watson

Program Description

The hydrogen pickup characteristics of zirconium alloys during corrosion in steam or water have been shown to be very sensitive to the composition of the alloys. Many of the beneficial elements, however, exhibit very low solubility in alpha-zirconium, i. e., iron, nickel, and chromium, and exist predominantly as intermetallic particles in the alloy. The role of these elements in hydrogen pickup should therefore be assessed in terms of their respective intermetallic compounds with zirconium rather than as elemental additions. It has been suggested in the literature that these compounds anodically polarize the zirconium matrix, thereby improving corrosion resistance, and cause depolarization of corrosion byproduct hydrogen. It has been stated that iron and nickel compounds have low hydrogen overvoltages in aluminum alloys and should depolarize

absorbed monatomic hydrogen at the surface.⁽²⁾

The possible role of the compounds in hydrogen pickup is therefore being studied in terms of their hydrogen overvoltages. Measurements will also be made on the same intermetallics which have been partially oxidized in order to more closely simulate the conditions which would exist on oxidized alloy samples.

Fabrication of Specimens

Specimens suitable for overvoltage measurements have been prepared by arc melting weighed amounts of high purity starting materials under an inert atmosphere. Specimens prepared to date are: Zr (crystal bar), Zr_2Ni , Zr_2Cu , ZrFe_2 , ZrV_2 and Zr - 90% Nb.

Difficulty has been encountered in cutting the ZrFe_2 because of the extreme brittleness of the alloy. Ultrasonic abrasive cutting may be necessary to prevent shattering of the specimen.

Overvoltage Apparatus

A preliminary overvoltage apparatus was constructed, and overvoltage measurements were made on Zr (crystal bar), Zr_2Ni , Zr_2Cu and Zr - 90 Nb. Data for the Zr - 90 Nb will be presented at a later date. Limitations of current density, electrolyte purity and scatter in the data resulted in the design and construction of an improved cell as shown in Figure 1. This cell is essentially a closed system containing both a Hildebrand type hydrogen electrode and a saturated $\text{Hg}/\text{Hg}_2\text{Cl}_2$ electrode. Improvements in capillary design, temperature control, stirring, and electrolyte purity have been achieved with this cell. A current density range from 10^{-5} amp cm^{-2} to 1 amp cm^{-2} is now available in controlled increments.

Measurement Technique

Prior to all measurements, the entire cell is cleaned with an aqueous solution of 50% HNO_3 followed by hot 1M H_2SO_4 and several washings with distilled water. The 1M H_2SO_4 electrolyte is purified by pre-electrolysis at 10^{-2} amp cm^{-2} for 24-48 hours. This operation removes impurities which might plate out during overvoltage measurements.

Figure 1. HYDROGEN OVERVOLTAGE CELL

Polished rectangular prisms with total surface areas ranging from 2 to 4 cm² are used as specimens. Each specimen is spot-welded to a 15 mil Pt lead wire and totally immersed in the electrolyte. Cathodic hydrogen charging for 30-60 seconds at a high current density ($\sim 10^{-2}$ amp cm⁻²) is used to reduce surface oxides on the specimen prior to measurements.

Overvoltage measurements at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ between a saturated calomel electrode and the intermetallic specimen are made with a modified General Electric recording potentiometer and calibrated with a Leeds and Northrup volt potentiometer. The potential at each current density is allowed to stabilize before measurements. At the lower current densities, only 2 to 3 minutes are required for stabilization, while at the high current densities stabilization times as great as 20 minutes are required. After the potential measurement at each current density is made, the polarizing current is shut off and the potential decay is measured with the recording potentiometer. Extrapolation of the decay curve to zero time is used to determine the reversible hydrogen potential.

Preliminary Results

The measured Tafel equations for the materials studied are:

$$\begin{array}{ll} \text{Zr} & \eta_c = 0.852 + 0.136 \log i \pm 0.005 \text{ v} \\ \text{Zr}_2\text{Cu} & \eta_c = 0.877 + 0.153 \log i \pm 0.005 \text{ v} \\ \text{Zr}_2\text{Ni} & \eta_c = 0.777 + 0.123 \log i \pm 0.005 \text{ v} \end{array}$$

where η_c is the cathodic hydrogen overvoltage and i is the current density obtained by dividing the measured current by the apparent surface area of the cathode.* The above equations are reasonably followed over the current density range 2×10^{-4} amp cm⁻² to 5×10^{-2} amp cm⁻² as shown in Figure 2. From the plot of these equations it may be seen that differences between the hydrogen overvoltage values are slight at low current densities but increase significantly at higher current densities. In an actual corrosion

* The Frumkin convention of positive values for cathodic overvoltage is used in these measurements.

Figure 2. HYDROGEN OVERVOLTAGE VERSUS CURRENT DENSITY FOR ZIRCONIUM AND ZIRCONIUM INTERMETALLICS

cell established between a large Zr matrix and microscopic intermetallic particles, it is likely that a rather high current density exists at the intermetallic even though the potential produced by the cell may be small. Thus the relation between hydrogen pickup in Zr alloys and hydrogen overvoltage of various phases is most significant at high current densities.

The new cell shown in Figure 1 will allow measurements at the current densities of interest.

The above Tafel equation is not mathematically proper since no significance can be attached to values of the intercept, i.e. (0.852, 0.877 and 0.777). A better form is

$$i = i_0 \exp (\alpha F \eta / RT) \quad (1)$$

in which i_0 is the current density at zero overvoltage, i is the current density at any overvoltage η , F is the value of the Faraday in coulombs, R is the gas constant, T is the absolute temperature and α which is known as the transfer coefficient may be determined from

$$b = \frac{2.303 R T}{\alpha F} = \frac{\partial \eta}{\partial \log i} \quad (2)$$

Solving for α and substituting into equation (1) we then have

$$i = i_0 \exp 2.303 \frac{\eta}{b} \quad (3)$$

In this form a relationship is expressed between the slope of the Tafel line, the intercept i_0 and the overvoltage η at any current density i . The Tafel plots expressed in this form for the materials investigated are:

Zr	$i = 7.04 \times 10^{-7} \exp 2.303 \eta / .136$
Zr ₂ Cu	$i = 1.86 \times 10^{-6} \exp 2.303 \eta / .153$
Zr ₂ Ni	$i = 4.79 \times 10^{-7} \exp 2.303 \eta / .123$

All further measurements will be reported in this form.

The Zr₂Ni alloy failed by spalling during the overvoltage measurements. In order to remove certain doubts concerning the failure mechanism, a second specimen was prepared by progressive polishing to 1 micron diamond dust, light chemical etching, and subsequent vacuum annealing at 800 C

for 22.5 hours. Following the heat treatment the specimen was lightly etched to remove surface contaminants. With the above treatment it was felt that residual stresses in the specimen were removed. The specimen was then made the cathode of the electrolytic cell. After approximately 46 minutes at various current densities, spalling and cracking was visually observed.

Chemical analysis revealed a large increase in the hydrogen content of the spalled specimen. A control specimen contained approximately 70 ppm hydrogen while the cathodically charged specimen contained 228 ppm. The surface concentration of hydrogen was considerably higher than 228 ppm, since X-ray diffraction revealed the presence of a second phase in the spalled particles. Presence of an extra set of diffraction lines indicates that a stable Zr_2Ni -hydride phase was probably formed by the cathodic hydrogen charging. It is likely that spalling observed was caused by the stresses generated at the interface of the Zr_2Ni and a non-equilibrium Zr_2Ni -hydride phase.

Cathodic charging of a Zr_2Cu intermetallic for over 2 hours at high current densities did not result in any visible spalling or cracking. An explanation for the spalling in Zr_2Ni versus none in Zr_2Cu will be presented at a later date.

Significance of Hydrogen Overvoltage

Hydrogen overvoltage is defined as the difference in potential between an electrode which is discharging hydrogen and the same electrode which is discharging hydrogen reversibly.* This reaction may be written

$$\eta_c = E_o - E_r$$

where E_o is the observed emf of the cell, E_r is the reversible emf, and η_c is the cathodic overvoltage.

The mechanism for the hydrogen discharge has been proposed to be:

* Overvoltage is sometimes defined as the difference in potential between an electrode which is discharging hydrogen and the steady state mixed emf of the cell.

or

The combination of steps A and B (known as the Volmer-Tafel mechanism) is essentially a discharge of a hydrogen ion to a hydrogen atom which remains adsorbed at the electrode surface, followed by a combination of adsorbed hydrogen to release hydrogen molecules. In this mechanism either A or B may be the rate-determining step in the hydrogen evolution reaction.

The combination of steps A and C is known as the Volmer-Horiuti mechanism in which the first step is followed by the discharge of a hydrogen ion to a hydrogen atom with a simultaneous combination of the metal hydride with the hydrogen to yield the diatomic hydrogen and the free metal. Theoretical calculations have been made by various workers to determine which of these steps is the rate-determining step in the discharge reaction. The criteria for determining which of the steps is rate-determining have been presented by Bockris as shown in Table I, where b is determined from equation (2), and ν from

$$\nu = \frac{-2 i_o F}{RT} \left(\frac{\partial \eta}{\partial i} \right)_{i \rightarrow 0} \quad (4)$$

Measurements of $\frac{\partial \eta}{\partial i} \rightarrow 0$ are difficult because of the low current densities required. However, b values are sufficient to determine that the slow or controlling mechanism of the hydrogen evolution reaction in the intermetallics studied to date is the hydrogen ion discharge at the electrode double layer (Step A) and not the desorption of the hydrogen at the electrode surface. Thus material with the lower overvoltage at a given current density will discharge atomic hydrogen more readily and at a greater rate than one with a higher overvoltage. Whether or not the

TABLE I (3)

CHARACTERISTIC VALUES OF DIAGNOSTIC CRITERIA IN THE HYDROGEN
EVALUATION REACTION

Mechanism		b 25°C	v
A slow	B fast	0.116	2
A fast	B slow	0.029	1
A slow	C fast	0.116	1
A fast	C slow	0.038	1

hydrogen atoms subsequently combine to form the molecule depends on the relative strengths of the metal-hydrogen bonds.

The metal hydrogen bonding energy may be seen to control the hydrogen overvoltage in the following manner. Assuming the Volmer-Tafel discharge reaction, we see that

Under steady state conditions, the rate of desorption of molecular hydrogen will be constant, but will be controlled by the MH bond strength. The higher the strength of the MH bonds, the lower will be the rate of gaseous hydrogen evolution. Representing the rate of atomic hydrogen discharge by the relative length of the arrows of the forward and reverse reactions, we have

The algebraic sum of iF and iR results in a Δi which represents the potential or overvoltage required to drive the reaction. In the case of a truly reversible reaction, $iF = iR$, and there is no overvoltage. If a material has particularly strong MH bonds, the MH concentration will increase, thus shifting the reaction in the reverse direction, i.e., increasing the magnitude iR . This in effect will decrease Δi and be manifested in a lower overvoltage.

This has been shown to be the case by Rüetschi and Delahay⁽⁴⁾. These authors have shown that a linear relationship exists between the overvoltage values of pure metals and their respective heats of adsorption of atomic hydrogen. Since hydrogen pickup during electrochemical measurements is directly related to the heat of hydrogen adsorption, and since the heat of adsorption is inversely proportional to the hydrogen overvoltage, it follows that hydrogen pickup should be inversely proportional to the hydrogen overvoltage.

Whether the above argument is true for oxidized cathodes and high

current densities (such as found during the corrosion of zirconium alloys) remains to be determined in the following phases of this work.

Further Work

Measurements of overvoltage will be made on ZrV_2 , ZrFe_2 and oxides of Zr, Zr_2Ni , Zr_2Cu , ZrFe_2 , ZrV_2 and Zr-90 Nb. If possible, some measurements will be made in a less acidic solution.

5. Properties of Oxides -- Oxygen Diffusion

D.L. Douglass, F.A. Watson

Program Description

It has been generally accepted by numerous investigators that the rate-controlling step in the corrosion and oxidation of zirconium alloys appears to be the diffusion of oxygen through the protective oxide film to the oxide-metal interface, at which point the reaction takes place. Studies of the steam oxidation of zirconium have included many alloys containing both lower and higher valent solutes than the parent metal. The subsequent improvement or decrease in oxidation resistance has been attributed to the change in anion vacancies, according to the Wagner-Hauffe theories, the change in vacancy concentration changing the diffusion rate of oxygen and thus the oxidation or corrosion rate. This approach has appeared very interesting and has shown that correlations exist, but unfortunately no data have been available for confirmation, and all treatments have therefore been speculative. It is the primary purpose of this subtask to determine the diffusion rate of oxygen through the pure oxide, to measure the dependence of diffusivity with vacancy concentration in the pure oxide, and to determine the effect of added solutes on both defect concentration and oxygen diffusion rates.

The rate of oxygen diffusion in the pure oxide was completed during the first quarter and comprised a portion of a paper presented by Dr. D. L. Douglass at the IAEA Conference on the Corrosion of Nuclear Materials in Salzburg, Austria, June 4-9, 1962. The work is being

prepared for distribution as a topical report to be issued during the next quarter. The conclusions are presented in the following section.

Experimental Results

Subtask 5-a: Diffusion of Oxygen in $\text{ZrO}_{1.955}$

1. The diffusion rate of oxygen in anion-deficient zirconia, $\text{ZrO}_{1.955}$, has been determined by the interface migration of stoichiometric oxide and is given by the equation

$$D = 0.055 \exp (-3,400 + 3100/RT)$$
2. The activation energy agreed very closely with values for the parabolic oxidation of zirconium in oxygen and in some cases with the value for oxidation according to a cubic rate law. The corrosion of crystal bar zirconium in water followed a cubic rate law and had an activation energy identical to that determined for oxygen diffusion in the anion-deficient zirconium oxide.
3. A grain boundary network of oxygen-saturated alpha zirconium formed during hot pressing and was almost entirely removed by subsequent vaporization in vacuum at 1900 C.
4. Oxidation of the as-pressed oxides resulted in preferential oxidation of the metallic phase with an associated volume change which caused intergranular shattering of the oxide. Heat-treated samples still exhibited an overwhelming propensity to very rapid grain boundary diffusion followed by slower lateral diffusion into the oxide grains.
5. A speculative mechanism for corrosion transition was suggested based on the presence of a thin film of a metallic phase in grain boundaries. The presence of alloying constituents in the oxide was offered as a means of lowering the eutectoid temperature in the zirconium-oxygen system.
6. A large difference in activation energies existed between this study and that for oxidation on non-stoichiometric $\text{ZrO}_{1.975}$ according to Aronson. The difference was attributed to space

charge effects in the very fine powders (about 2×10^{-5} cm diameter) used by Aronson. The space charge layer required an additional energy term for penetration by both electrons and oxygen vacancies.

REFERENCES

1. Private communication, S. Dalgaard, AECL, Chalk River, Ontario, Canada.
2. Dräley, J. E. and Ruther, W. E., Corrosion, 12, 480 (1956).
3. J. O'M. Bockris, Annual Review of Phys. Chem., Vol. 5, p.483 (1954).
4. P. Rüetschi and P. Delahay, Journal of Chemical Physics 23, 195,(1955).

III PROGRAM STATUS

Task B

Target properties have been determined and approved by the contracting officer (May 7, 1962).

The alloy field has been selected and approved by the contracting officer (May 7, 1962).

Fabrication of the alloys is 60% complete and will be 100% complete by August 15, 1962.

Corrosion testing is anticipated to begin August 15, 1962, two weeks behind the original schedule.

Hydrogen analyses are anticipated to begin August 15, 1962 as originally scheduled.

Mechanical testing is anticipated to begin on August 15, 1962 as originally scheduled.

Statistical analysis of test results is not scheduled until later this year.

Task A

Samples of non-stoichiometric zirconium oxide have been prepared and oxygen diffusion kinetics determined (reported at IAEA Symposium Salzburg Austria, June 9, 1962). This work anticipates the original schedule by approximately three months.

Hydrogen overvoltage on four phases found in zirconium alloys have been initiated roughly three months ahead of the original schedule.

Film stripping techniques necessary for corrosion film composition studies have been developed.

IV TECHNICAL LIAISONTechnical Meetings

AEC 11th Annual Corrosion Symposium, May, 1962

H. H. Klepfer, D. L. Douglass

IAEA Corrosion Symposium, Salzburg, June, 1962

D. L. Douglass

Visits to Other Laboratories

Saclay, Metallgesellschaft, Siemens-Schukertwerke, Harwell, June, 1962.

D. L. Douglass

Visitors to Vallecitos

J. N. Wanklyn, Harwell, April, 1962

C. Tyzack, Culceth, June, 1962

W. R. Thomas, AECL, June, 1962

(P. Berge, Euratom, July, 1962)

ReportsPapers

"Corrosion Mechanism of Columbium, Zirconium, and Their Alloys. I.
Diffusion of Oxygen in Columbium Pentoxide and Zirconium Dioxide"

D. L. Douglass, June 9, 1962, IAEA Conference on the Corrosion of Nuclear
Materials.