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PROCEEDINGS OF THE USAEC SYMPOSIUM ON
ZIRCONIUM ALLOY DEVELOPMENT—CASTLEWOOD,
PLEASANTON, CALIFORNIA, NOVEMBER 12-14, 1962

Compiled by
H. H. Klepfer

November 30, 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

UNITED STATES - EURATOM JOINT RESEARCH AND DEVELOPMENT PROGRAM

VOLUME I

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USAEC SYMPOSIUM ON
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UNITED STATES — EURATOM JOINT RESEARCH AND DEVELOPMENT PROGRAM

VALLECITOS ATOMIC LABORATORY

GENERAL ELECTRIC
ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

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"INTRODUCTION"

The United States and the European Atomic Energy Community (Euratom), on May 29, and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U. S. - Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

The work described in this report represents the Joint U. S. - Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in western Europe and the United States.

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- The Role of Deformation Twinning in the Plastic Deformation of Zirconium - R. E. Reed-Hill
- A Preliminary Examination of the Formation and Utilization of Texture and Anisotropy in Zircaloy-2 - M. L. Picklesimer
- Tensile Properties of Zircaloy with Oriented Hydrides - R. P. Marshall and M. R. Louthan
- The Oxidation of Zirconium Binary Alloys in 700°C Oxygen for Times up to 200 Days - R. Misch and C. Van Drunen
- Some Effects of Pressure on the Oxidation of Zircaloy-2 in Steam and Oxygen - B. Cox
- The Corrosion of Zircaloy-2 Fuel Element Cladding in a Boiling Water Reactor Environment - R. C. Nelson
- Electrical Properties of ZrO_2 Corrosion Films - D. W. Shannon
- Solute Distribution Between Corrosion Films and Alloy Substrate - D. L. Douglass and M. E. Urata
- Note on the Defect Structure of ZrO_2 and HfO_2 - P. Kofstad and D.J. Ruzicka
- Preliminary Experiments on the Use of AC Polarography Techniques in the Determination of Hydrogen Transport Mechanisms in Zirconium Alloy Oxide Films - T. Brush
- Hydrogen Overvoltage on Zirconium Intermetallics - J. S. Armijo

INTRODUCTION

This report presents the proceedings of an international working symposium on zirconium alloy development sponsored by the U.S. Atomic Energy Commission. The symposium was held November 12-14, 1962 at Castlewood, Pleasanton, California with the Vallecitos Atomic Laboratory of General Electric's Atomic Power Equipment Department as host.

The first session of the symposium was a review of the development of zirconium alloys already commercially available and in reactor service. In subsequent sessions research workers were invited to present research in progress pertinent to efforts to develop additional zirconium alloy compositions. Those who responded to this invitation to participate in the symposium are indicated on the agenda for the symposium which appears on the following pages.

It should be emphasized that the papers presented were research-in-progress reports intended to indicate the current activity in the field of zirconium alloy development and were not intended to present a comprehensive picture of the state of the art. The papers are printed here just as furnished in reproducible form by the authors at the time of the conference. The only editorial work performed was that done in arranging the order of the papers for the symposium agenda and in providing for page numbers and graphic reproduction. (This work was performed under AEC Contract AT(04-3)-189, Project Agreement 24, Joint U.S.-Euratom Research and Development Program.)

In an attempt to summarize the highlights of the symposium, the author submits the following two paragraphs based on notes taken at the time:

With regard to new alloy compositions, the Zircalloys are still clearly the most applicable for water-cooled reactor fuel cladding. Development of Zr-Nb (and Zr-Nb-Sn) alloys for water-cooled reactor pressure tubes is proceeding rapidly and draws on a broad base of thorough physical metallurgy. Recent work has not challenged the British Zr-Cu-Mo alloys for carbon dioxide cooled reactor components. By far the most controversy was found in reports on the efforts to

develop zirconium base alloys for steam-cooled reactor components; primary candidates for suitable dilute alloying additions appear to be Nb, Cu, Fe, Cr, perhaps Ni and V, and surprisingly Ca, Y, and Ce.

Basic corrosion studies in support of these alloy developments show new emphasis on determining the properties of the corrosion films. The composition, electrical properties, and defect structure of the films are beginning to receive detailed attention. The prevalent theory that zirconium and zirconium alloy corrosion proceeds by bulk diffusion of oxygen via anion vacancies is being strongly challenged. No theory has been put forth which explains or predicts the effect of various alloying additions on the corrosion kinetics or on corrosion hydrogen take-up. Pertinent to all zirconium alloy compositions is new research emphasis aimed at the control of texture in mill products to improve both mechanical properties and to improve resistance to hydride embrittlement.

H. H. Klepfer, Symposium Chairman
Pleasanton, California
November 27, 1962

AGENDA

USAEC ZIRCONIUM ALLOY DEVELOPMENT
SYMPOSIUM

Monday - November 12

Registration

Symposium Opening - S. Christopher (USAEC, Wash.)

SESSION I - HISTORICAL REVIEWS - H. H. Klepfer, Chairman

The Development of the Zircalloys - S. Kass (BAPD)

The Development of Zirconium Alloys for Pressure Tubes in Water-Cooled Power Reactors - W. R. Thomas (AECL)

SESSION II - CURRENT DEVELOPMENT EFFORTS - W. R. Thomas, Chairman

An Investigation of Zirconium Alloys for Resistance to Carbon Dioxide Corrosion - W. A. Maxwell (GNEC)

Development of Zr-Nb-Sn Alloys for Reactor Applications - J. C. Tverberg and H. Richter (HAPO - Metallgesellschaft)

Research on Alpha-Active Eutectoid Zirconium Alloys - R. P. Syre (Pechiney)

Development of Improved Zirconium Alloys for Use in Superheated Water and Steam - D. Weinstein (ARF)

Corrosion Resistance of Improved Zirconium Alloys in High Temperature Steam - U. Rösler (Siemens-Schuckertwerke)

Zirconium Alloy Design for Steam Service - H. H. Klepfer (Vallecitos)

SESSION III - BASIC WORK - Physical Metallurgy and Mechanical Properties - R. F. Heheman and, M. L. Picklesimer, Chairmen

A Metallographic Determination of the Zirconium-Niobium Diagram - C. E. Lundin and R. H. Cox (Denver Research Institute)

Transformations in Zirconium-Niobium Alloys - R. F. Hehemann (Case Institute)

The Effects of Heat Treatment on the Mechanical Properties of Zirconium-2½% w/o Niobium Alloy - J. Winton and R. A. Murgatroyd, presented by E. LeSurf (Culcheth)

The Role of Deformation Twinning in the Plastic Deformation of Zirconium - R. E. Reed-Hill (University of Florida)

A Preliminary Examination of the Formation and Utilization of Texture and Anisotropy in Zircaloy-2 - M. L. Picklesimer (ORNL)

Tensile Properties of Zircaloy with Oriented Hydrides - R. P. Marshall
and M. R. Louthan (Savannah River)

Wednesday - November 14

SESSION IV - BASIC WORK - Corrosion - D. L. Douglass, Chairman

The Oxidation of Zirconium Binary Alloys in 700°C Oxygen for Times
up to 200 Days - R. Misch and C. Van Drunen (Argonne)

Some Effects of Pressure on the Oxidation of Zircaloy-2 in Steam
and Oxygen - B. Cox (Harwell)

The Corrosion of Zircaloy-2 Fuel Element Cladding in a Boiling
Water Reactor Environment - R. C. Nelson (Vallecitos)

Electrical Properties of ZrO_2 Corrosion Films - D. W. Shannon
(Hanford Laboratories)

Added paper in discussion - Preliminary Experiments on the Use of
AC Polarography Techniques in the Determination of Hydrogen Transport
Mechanisms in Zirconium Alloy Oxide Films - T. Brush (APED)

SESSION V - BASIC WORK - Corrosion - B. Cox, Chairman

Solute Distribution Between Corrosion Films and Alloy Substrate -
D. L. Douglass (Vallecitos)

Note on the Defect Structure of ZrO_2 and HfO_2 - P. Kofstad and
D. J. Ruzicka (Central Institute for Industrial Research - Oslo)

Hydrogen Overvoltage on Zirconium Intermetallics - J. S. Armijo
(Vallecitos)

THE DEVELOPMENT OF THE ZIRCALOYS

by

Stanley Kass

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Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

Work performed under
AEC Contract AT-11-1-GEN-14

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The Development of the Zircalloys

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(AT-11-1-GEN-14)

ABSTRACT

The experimental work leading to the development of Zircalloys-1, -2, -3, and -4 are reviewed. The corrosion properties of Zircalloys-2 and -4 in high temperature water and steam and the effects of composition, heat treatment, and water chemistry upon oxide film formation and hydrogen absorption during corrosion are discussed.

The Development of the Zircalloys

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Pittsburgh, Pennsylvania

(AT-11-1-GEN-14)

Constructional materials in water-cooled and moderated nuclear reactor cores serve many functions:

1. As cladding to prevent the access of the water coolant to the fissionable fuel and to prevent the release of fission products produced in the fuel to the plant system,
2. As a structural member to support the reactor core and to prevent fuel element distortion from the various forces or stresses imposed as a result of fission processes within the fuel,
3. As a heat exchange surface which in application may be required to transfer heat at extremely high rates.

The materials, therefore, must exhibit good corrosion resistance, adequate strength properties, high thermal conductivity. Lastly, the materials should possess a low thermal neutron capture cross section so that maximum economies in fuel costs may be realized.

Of all the conventional structural materials, only aluminum and magnesium meet the low cross section requirements; however, at elevated temperatures, both materials fail to meet the requirements of strength and corrosion resistance. Beryllium also appeared to hold some promise, but was rejected because of the high cost of the metal due to the scarcity of the ore and difficult fabrication processes coupled with poor mechanical properties and the helium buildup during irradiation. In contrast, zirconium ores are plentiful and the fabrication costs are

not prohibitive. Finally, the mechanical properties were demonstrated to be adequate for nuclear applications. The above combined with the very low (0.18 barns) cross section to thermal neutrons led to the selection of zirconium as a material for application in water-cooled and moderated nuclear reactors. Very little, however, was known about the corrosion performance of the metal in high temperature water and steam. A program was begun to develop information on the corrosion resistance of zirconium and its alloys. This program produced a family of zirconium-base alloys--the Zircalloys--which has seen extensive application in pressurized water reactors and has taken a place among the materials of technical importance.

The impetus and direction for the development of the Zircalloys was furnished by the Naval Reactors Branch and the Pittsburgh Naval Reactors Office of the U. S. Atomic Energy Commission. The early work culminating in the establishment of Zircaloy^s*-1, -2, and -3 was performed in the laboratories of the U. S. Bureau of Mines at Albany, Oregon, Argonne National Laboratory, the Metallurgical Laboratory of the Massachusetts Institute of Technology, Battelle Memorial Institute, Iowa State College, Oak Ridge National Laboratory, and the Bettis Atomic Power Laboratory of the Westinghouse Electric Corporation.

The scope of this review is to trace the development of the Zircalloys from the high purity Van Arkel metal through Zircalloys-1, -2, -3, and -4.

A. Unalloyed Zirconium

The first zirconium material available in large quantity lots for arc-melting, fabricating to strip and subsequent corrosion studies was crystal bar (Van Arkel process) zirconium. Extended corrosion tests in hot water and steam ranging from 500 to 750 F revealed that the material exhibited very variable properties. Some ingots would exhibit black adherent oxide films, which would remain adherent for

* U. S. Patent No. 2,772,964.

a considerable time in test. Other ingots would exhibit white oxides and extensive spalling after very short exposures; lastly, other ingots exhibited corrosion characteristics between the above two extremes. The kinetics of the reaction of zirconium with water at elevated temperatures were thus resolved into two distinct modes. The initial mode is characterized by the formation of a thin adherent corrosion product, exhibiting interference colors or a black appearance. After a period of time, a new and more rapid corrosion rate sets in, coincident with the formation of a white, non-adherent oxide. Figure 1 summarizes the weight gain - time information from a large number of arc-melted and rolled crystal bar zirconium samples. These curves represent only high quality zirconium since the materials had been previously screened by corrosion testing and chemical analysis. Each curve for Group A (triangle symbols) represents in excess of 100 specimens, each from a different ingot. The curves for Group B (circular symbols) represent specimens selected at random from about 2000 specimens tested. It will be noted that none of the specimens tested at 600 F or below exhibited accelerated corrosion; however, at 680 F a large number of the specimens exhibited rapid corrosion rates as indicated by the cross-hatched bands. After 254 days 32% of the original samples failed.

The impurity content of arc-melted crystal bar zirconium has a very marked effect upon its corrosion resistance to hot water. The effect of nitrogen upon the corrosion characteristics is very pronounced. The curves shown in Figure 2 are for crystal-bar nitrogen samples. It will be noted that samples containing more than 0.004% nitrogen (E&F) exhibit rapid corrosion rates within very short times in 600 F water. Nitrogen contents greater than 0.0130% result in complete disintegration.

Another factor contributing to accelerated corrosion of crystal-bar zirconium is brought about by mechanical operations giving rise to a layer of disturbed metal

FIG. 1-1. CORROSION OF ARC-MELTED CRYSTAL BAR ZIRCONIUM

THE EFFECT OF NITROGEN CONTENT UPON THE CORROSION RESISTANCE OF ZIRCONIUM. SAMPLES WERE MADE BY POWDER METALLURGY TECHNIQUES.

FIG. 1-2.

at and for some distance below the surface. This factor may be overcome by chemically removing the disturbed layer by etching in an $\text{HNO}_3\text{-HF-H}_2\text{O}$ solution. However, surface contamination of the freshly etched specimen can induce accelerated corrosion if all residual etchant is not removed from the surfaces prior to corrosion exposure. Figure 3 illustrates the accelerated corrosion that occurred after 3 days in 680 F water on the surfaces of zirconium specimens that were contaminated with residual etchant solution.

From the foregoing it can be seen that unalloyed zirconium exhibits many undesirable properties; chiefly, those attributed to minor amounts of impurities, surface condition, and improper removal of all residual etchant. Furthermore, the great variability of the quality of crystal bars from lot to lot gave additional impetus towards the development of zirconium-base alloys. Additional aims in alloying were to make it possible to employ the less expensive Kroll process sponge zirconium than the iodide process material as well as to obtain mechanical property improvements.

B. Zirconium-Tin Alloys

It was discovered independently by Battelle Memorial Institute and Iowa State College that the addition of tin to "impure" zirconium tends to overcome the deleterious effects of nitrogen and to a lesser extent that of carbon and aluminum. Figure 4 and Figure 5 illustrate the effects. In Figure 4 the data from two sets of tin-bearing alloys prepared from pure crystal bar starting stock are presented. Curve A represents one series while Curve B represents the second series. It can be readily noted that the weight gains increase with increasing tin content. Figure 5 shows the effect of tin upon the corrosion resistance of arc-melted sponge zirconium containing about 60 ppm nitrogen where an optimum tin content is observed. On the low side of the optimum tin content, the weight gain values

FIG. 1-3. ACCELERATED CORROSION ON ZIRCONIUM SURFACES PRODUCED BY INCOMPLETE REMOVAL OF HF-HNO_3 ETCHANT

FIG. 1-4. EFFECT OF TIN CONTENT UPON CORROSION RESISTANCE OF CRYSTAL BAR ZIRCONIUM

FIG. 1-5. EFFECT OF TIN CONTENT UPON CORROSION RESISTANCE OF SPONGE ZIRCONIUM

increase toward the high values representative of the unalloyed sponge. On the high tin side, the weight gains increase with tin. A second beneficial effect brought about by the addition of tin to zirconium was observed in the kinetics for the reaction in hot water. Initially, zirconium-tin alloys and unalloyed zirconium behave similarly in that an initial period of low corrosion is followed by a period of accelerated corrosion. Unlike unalloyed zirconium, however, the oxide formed on zirconium-tin alloys during the period of accelerated corrosion is adherent and flaking may not occur until weight gains of several hundred milligrams per square decimeter are reached.

The amount of tin necessary to impart optimum corrosion resistance to "impure" zirconium was found to be dependent upon the nitrogen content of the alloy. Estimations for the nitrogen tolerance limits were made by workers at Massachusetts Institute of Technology and it was recommended that an alloy containing 2.5% tin which could counter-affect about 700 ppm nitrogen be studied. This alloy-- sponge zirconium plus 2.5% tin-- was known as Zircaloy-1. A program was then undertaken to determine whether the unavoidable variations in impurity content from lot to lot of sponge zirconium had any significant effect on the corrosion resistance of the alloy. The base materials were selected from 50 random lots of sponge zirconium. Fifty 100-gram ingots of the 2 $\frac{1}{2}$ % tin-sponge zirconium alloy were double arc-melted, fabricated, machined, etched, and corrosion tested in 600 and 650 F water. After about 100 days exposure the samples tested in 600 F water were satisfactory; however, many of those tested at 650 F showed very high weight gains (values as high as 700 mg/dm² were not uncommon) although the oxide films were adherent. Data accumulated from these 50 ingots strongly suggested that the presence of iron, nickel, or chromium, singly or in combination in the zirconium-tin alloy, greatly increased the corrosion resistance of the binary alloy. Figure 6 illustrates the effect of iron content upon the

FIG. 1-6. EFFECT OF IRON CONTENT UPON THE INCIDENCE OF ACCELERATED CORROSION ON CRISTAL BAR - 2.5% TIN ALLOY
68 DAYS IN 600 F WATER

incidence of accelerated corrosion in specimens from 26 ingots of the zirconium-2.5% tin alloy after 68 days in 600 F water.

C. Zirconium-Tin-Iron-Nickel-Chromium Alloys

Since the addition of tin to zirconium did not appear to exert its full beneficial effect unless iron, nickel, or chromium were present, the alloy development program was extended to evaluate the roles of these elements upon the corrosion characteristics of zirconium.

Figure 7 summarizes the 600 and 680 F water and 750 F - 1500 psi steam corrosion behavior of zirconium-2.5% tin alloys containing small amounts of iron, nickel, or chromium, indicating the effectiveness of the ternary alloying element in enhancing the corrosion resistance of the binary alloy. Curves similar to Figure 7 were obtained from work evaluating the behavior of binary alloys with iron, nickel, or chromium. Thus, the functions of the alloying elements iron, nickel, and chromium appear to be similar. These elements exert a favorable effect upon the corrosion resistance of zirconium in delaying the initiation of accelerated corrosion in hot water as well as in 750 F - 1500 psi steam.

Further investigations of the nitrogen tolerance of zirconium-tin ternary alloys with iron, nickel, or chromium showed that the tolerance limits for the ternary alloys were higher than for the binary zirconium-tin alloy. Concurrently, the Albany station of the U. S. Bureau of Mines had made a number of refinements to the Kroll process for the preparation of sponge zirconium that yielded a product of lowered nitrogen content. The above information coupled with the knowledge that the corrosion rates of zirconium-tin alloys decrease with decreasing tin content (Figure 4) lead to investigations into the properties of zirconium-1.8 w/o tin alloys containing additions of iron, nickel, or chromium. The data from these experiments are plotted in Figure 8. The alloys represented were arc-melted from a

FIG. 1-7. EFFECT OF Fe, Ni, Cr ADDITIONS ON ARC-MELTED SPONGE
2.5% Sn ALLOYS

CORROSION OF Zr-1.8% Sn-BASE TERNARY ALLOYS WITH Fe, Ni, AND Cr.

single batch of zirconium sponge containing 30 ppm N₂, 210 ppm C, 40 ppm Al. The unalloyed base material and the 1.8% tin alloy failed after 14 days in 680 F water and after 4.5 days in 750 F - 1500 psi steam. It is seen that nickel and iron are equally effective in improving corrosion resistance and both are more effective than chromium. It should be noted that the curves in the figure resulting from the steam tests reflect the same behavior as the water tests.

D. Zircaloy-2

The composition of Zircaloy-2 was then fixed as follows:

1. Tin Content - 1.5%

Since Zircaloy-1 proved to be unsatisfactory in regard to corrosion resistance, the tin content was dropped to 1.5% from 2.5%. The amount in Zircaloy-2 is sufficient to neutralize the effect of about 1000 ppm of nitrogen, which is considerably more than would be expected in zirconium sponge material.

2. Iron Content - 0.12%

Data from Westinghouse, Bureau of Mines and M.I.T. indicated that small quantities of iron increased the corrosion resistance of zirconium. An optimum value of 0.22% Fe was indicated from binary alloy studies, but since Zircaloy-2 contains other beneficial elements, and the total alloy content should be kept to a minimum to insure ease in fabrication, the iron content was fixed at 0.12%.

3. Chromium Content - 0.1%

The chromium content of Zircaloy-2 is 0.1%. It has been found that chromium is beneficial in preventing corrosion of zirconium. Although data on binary zirconium-chromium alloys indicated the corrosion resistance of zirconium increases with increasing chromium content, the amount of chromium was kept at 0.1% so that the hardness of the alloy would not be increased excessively.

4. Nickel Content - 0.05%

Nickel was also shown to increase the corrosion resistance of zirconium exhibiting its greatest influence in extending the life of zirconium alloys in high temperature steam. An optimum value is 0.25% Ni for binary zirconium-nickel alloys. Since Zircaloy-2 contains other beneficial elements and since total alloy content had to be kept at a minimum to insure easy fabricability, the nickel content was fixed at 0.05%. The complete specification range for the alloy is presented in Table I.

TABLE I - Chemical Composition of Zircaloy-2

<u>Alloying Element</u>	<u>Weight %</u>
Tin	1.20 to 1.70
Iron	0.07 to 0.20
Chromium	0.05 to 0.15
Nickel	0.03 to 0.08

The sum of iron, chromium, and nickel must fall within the range 0.18 to 0.38 percent.

Maximum Impurity Limits

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Al	75	H	25
B	0.5	Mn	50
Cd	0.5	N	80
C	270	Si	200
Co	20	Ti	50
Cu	50	W	100
Hf	200	U Total	3.5

The most important single property of Zircaloy-2 is its excellent corrosion resistance in high temperature water, in which respect it is vastly superior to unalloyed zirconium. The corrosion is characterized by the formation of a tightly adherent zirconium dioxide film which initially follows a quasi-cubic rate law. After an initial corrosion period, a new rate law, approximately linear, sets in.

Since the corrosion-produced oxide is adherent and remains on the surface of the metal, the increase in weight is a measure of the amount of corrosion. In Figure 9 the weight gain for vacuum-melted Zircaloy-2 is plotted as a function of time on logarithmic scales for exposure in 550, 600, and 680 F water and in 750 F steam. A transition in kinetics is noted at both 680 F (~100-120 days) and 750 F (~40 days). Preliminary estimates for transition in 600 F water is about 600 days and about 1800 days in 550 F water. Zircaloy-2 appears to follow the same type of kinetics in 750 F steam at 1500 psi as it does in water at lower temperatures at saturation pressure; however, the 750 F test does not always predict behavior in lower temperature water. This apparent discrepancy between the 750 F steam test and water tests will be discussed in later sections as will be discussed the corrosion at temperatures greater than 750 F. The corrosion properties of the alloy are not sufficiently sensitive to composition so that reasonable variations about the nominal need not be of concern in the practical sense. (Note Figures 10 and 11.

The water corrosion of Zircaloy-2 is only slightly affected by prior heat treatment; however, the resistance to steam at 750 F and above can be markedly decreased by heat treatments in the two-phase alpha-plus-beta field, or by slowly cooling through the alpha-plus-beta field. Figure 12 illustrates the percentage change in the 14-day 750 F - 1500 psi steam weight gain value obtained from Zircaloy-2 specimens heat treated for 8 hours and furnace cooled from various temperatures. Figure 13 illustrates the dependence of the 14-day, 750 F - 1500 psi steam weight gain upon the rate of cooling through the two-phased region.

The corrosion resistance of Zircaloy-2 at temperatures greater than 750 F has not been studied as extensively as the behavior at temperatures up to and including 750 F. The preponderance of data, however, shows that the alloy exhibits properties ranging from adherent oxide formation to complete disintegration within a very short period of time. Figure 14 shows the phenomenon and also

FIG. 1-9. WEIGHT GAIN—TIME CURVES
FOR THE CORROSION OF ZIRCALLOY-2

FIG. 1-10.

FIG. 1-11.

FIGURE -12

FIG. 1-13. EFFECT OF COOLING RATE ON 14-DAY 750 F, 1500 psi STEAM WEIGHT GAIN OF ZIRCALOY -2

FIG. 1-14. CORROSION BEHAVIOR OF ZIRCALOY-2 IN HIGH-TEMPERATURE WATER AND STEAM

illustrates the influence of metallurgical structure upon the high temperature steam corrosion behavior. At 950 F only those samples quenched from the beta phase region (~1900 F) exhibited adherent oxides; but spalling at corners, edges, etc., was evident after three weeks exposure. All alpha or alpha-plus-beta-treated specimens spalled after only one day of test. At 850 F the samples alpha+beta-treated spalled after 2 days of test, but the alpha-annealed or beta-quenched materials showed adherent oxides. Some preliminary experiments were performed at 1150 F. All samples tested at 15 psi showed adherent oxides until 6 days of test; replicate samples, however, tested at 1500 psi, disintegrated completely with 24 hours exposure.

E. Zircaloy-3

In the spring of 1953 a new development program was undertaken to develop new zirconium alloys having corrosion resistance superior to the corresponding properties of Zircaloy-2. This new program, which culminated in the alloy "Zircaloy-3", was not dictated by any, at that time, known serious deficiency in the properties of Zircaloy-2, but by the desire to improve the alloy. For example, an alloy was desired which would have improved corrosion resistance in low temperature (~600 F) water; another desirable property of the alloy would be to show improved fabricability as measured by ductility. The basic program brought forth three alloys for consideration. The alloy compositions and designations are as follows:

Zircaloy-3A	0.25 w/o tin, 0.25 w/o iron
Zircaloy-3B	0.50% tin, 0.40% iron
Zircaloy-3C	0.50% tin, 0.20% iron, 0.20% nickel

Figure 15 depicts the corrosion behavior of the alloys in 750 F - 1500 psi steam. The post-transition rate of all Zircaloy-3 alloys is considerably lower than that of Zircaloy-2. Among the three alloys composition A is superior. All

ZIRCALOY-3, AVERAGE OF 4 SAMPLES FROM EACH OF 16 INGOTS

FIG. 1-15. CORROSION OF ZIRCALOYS 2 & 3 IN 750 °F STEAM (1500 PSI)

SPECIMENS FURNACE COOLED FROM 775 °C

alloys, however, exhibited strengths approximately 75% of that of Zircaloy-2

Concern over the corrosion resistance of Zircaloy-3 first occurred in the fall of 1956 when test results were obtained from the first lot of commercially-produced ingots. Prior to that time, there had been almost 100% acceptance of Zircaloy-2 and no indication of trouble had been revealed in a very extensive development program. The trouble with Zircaloy-3 manifested itself in the form of white corrosion product occurring in local areas strung out in the rolling direction (stringers). Subsequent examination of Zircaloy-2 strip products fabricated by the same techniques as the Zircaloy-3 strip products, showed the presence of faint gray-white stringers. The principal difference was that the Zircaloy-2 stringers were considerably smaller in size and more uniformly distributed. Further experimental work showed the mechanisms of stringer formation in the two alloys were different. For Zircaloy-3, the stringers were caused by a segregated grain boundary precipitate. Zircaloy-2 contained less precipitate, undoubtedly due to the broadening of the alpha solubility limit by the larger amount of tin present (1.5% Sn for Zircaloy-2 vs 0.25 Sn for Zircaloy-3). The stringers in Zircaloy-2 were found to be related to the gas voids formed in the metal during inert atmosphere melting. Subsequent experimentation showed that vacuum arc-melting techniques greatly minimized the occurrence of stringers in Zircaloy-2. Furthermore, beta quenching proved to be an effective remedial treatment for minimizing the stringer effect in Zircaloy-3.

Since Zircaloys-2 and -3 exhibit similar water corrosion properties and the remedial measures for minimizing the occurrence of stringers in Zircaloy-2 were easier to apply (vacuum melting) the application of Zircaloy-3 was minimized.

F. The Nickel-Free Zircaloys--Zircaloy-4 and Nickel-Free Zircaloy-2

The successful operation of pressurized water reactors employing Zircaloy-2 cladding, the extensive out-of-pile corrosion testing in degassed, neutral water

and the lack of any apparent irradiation effect on corrosion rate all indicate that oxide film formation should not be a Zircaloy-2 cladding corrosion problem. However, hydrogen pickup by the cladding during aqueous corrosion has been shown to be a potential limit to the useful life of the alloy. All zirconium alloys react with water to form the corrosion product zirconium dioxide and hydrogen. Although it was observed as early as 1953 that zirconium, Zircaloy-1, and Zircaloy-2 absorb hydrogen during corrosion and that the quantity of hydrogen absorbed was proportional to the amount of corrosion and that small quantities of hydrogen exert embrittling effects upon the mechanical properties of zirconium, experience showed that the amount of hydrogen absorbed was small. It was realized that an undesirable situation existed; however, it was believed that harmful effects would not be evident in short-lived reactors.

Subsequently, data obtained on the behavior of defected Zircaloy-2 clad UO_2 fuel rods in in-pile loop tests indicated that the following conditions are necessary to initiate hydriding failures: a cladding defect, a small diametrical clearance between the fuel and the cladding, a high external surface temperature, and a high heat flux. Failure occurs when the coolant enters the fuel rod through the defect; when the reactor is raised to power, the coolant reacts with the Zircaloy-2 or the UO_2 enriching the steam with hydrogen. This hydrogen enrichment produces accelerated hydriding.

Concurrently, it was demonstrated in both out-of-pile and in-reactor experiments that the hydrogen absorption of zirconium alloys is enhanced when nickel is present in the alloy.

In view of the above observations, it was considered prudent to initiate programs to re-evaluate the Zircaloy-2 composition, especially in respect to the nickel content and to determine the effect of coolant chemistry upon the hydriding of zirconium.

Studies to determine the effects of coolant chemistry upon the hydriding of zirconium alloys have produced a number of interesting observations.

1. Experiments conducted with Zircaloy-2, nickel-free Zircaloy-2, and Zircaloy-4 in lithium hydroxide solutions at 680 F showed that the corrosion characteristics of the alloys are independent of LiOH concentration up to levels corresponding to pH 11.3 (0.002M) but is significantly reduced at concentrations of pH 11.7 (0.005M) and higher. The hydrogen absorption characteristics as gauged by percent theoretical, however, were found to be constant at all LiOH concentrations and were consistent with neutral water exposure. The data indicate that no accelerated corrosion or hydrogen pickup of the Zircaloy cladding is to be expected in reactors using LiOH as a means of crud control if the pH is maintained below pH 11.3 and if there are no crevice regions wherein LiOH can concentrate.

2. Experiments conducted in the early 1950's demonstrated the deleterious effects of fluoride ion in the corrosion media upon the corrosion resistance of zirconium and its alloys; however, no information upon hydrogen absorption was developed. Recent experiments have shown that small amounts of fluoride ion (~10 ppm) can seriously affect the corrosion and hydrogen pickup of Zircaloy-2 during the first 7 days exposure in 572 F water. For example, when F^- was absent 5-11 ppm of hydrogen was absorbed by the Zircaloy-2, but when 10 ppm F^- was added to the water 22-42 ppm H_2 was absorbed.

3. Figure 16 shows the effect of hydrogen overpressure on the hydrogen absorption of Zircaloy-2 and Zircaloy-4 after two weeks exposure in 650 F water. The absorption of Zircaloy-2 is noted to increase linearly with applied pressure (500 psi increments) or increasing hydrogen content of the water. The hydrogen absorption for Zircaloy-4 is not only less than that of Zircaloy-2 but is relatively insensitive to the hydrogen content of the water. Dynamic corrosion.

tests with replicate materials tested at 615 F in pH 10.0 LiOH under conditions of 0 and 50 H₂ cc/kilo H₂O have confirmed the observation of the increased hydrogen absorption with increased hydrogen content of the water and that Zircaloy-2 is more sensitive to the hydrogen concentration of the water than Zircaloy-4.

4. A number of corrosion tests are being conducted to evaluate the role of dissolved oxygen upon the corrosion and hydrogen absorption characteristics of the Zircalloys. All tests have produced a common result: hydrogen pickup is markedly decreased by the presence of oxygen in the corrosion medium. For example, Zircaloy-4 shows 18% theoretical hydrogen absorption after 200 days in 680 F degassed water, but only 4% when the water is pressurized to 1000 psi with oxygen.

The results of the program re-evaluating the Zircaloy-2 composition produced two modifications of Zircaloy-2--nickel-free Zircaloy-2 and Zircaloy-4. In these modifications (Table II) the nickel concentration was fixed at a maximum impurity level consistent with the values in current raw materials. The first alloy, nickel-free Zircaloy-2 is essentially Zircaloy-2 without the nickel addition. The second alloy, Zircaloy-4, contains the same chromium and tin levels as Zircaloy-2 but the iron content has been increased to compensate for the removal of nickel.

TABLE II - Chemical Compositions of Zircalloys-2 and -4

<u>Element</u>	<u>Zircaloy-2*</u>	<u>Nickel-Free Zircaloy-2</u>	<u>Zircaloy-4**</u>
Sn	1.20 to 1.70%	1.20 to 1.70%	1.20 to 1.70%
Fe	0.07 to 0.20%	0.12 to 0.18%	0.18 to 0.24%
Cr	0.05 to 0.15%	0.05 to 0.15%	0.07 to 0.13%
Ni	0.03 to 0.08%	0.007% max.	0.007% max.

* Sum Fe, Ni, and Cr in Zircaloy-2 must range between 0.18 and 0.38%.

** Sum Fe and Cr in Zircaloy-4 must be 0.28% min.

The corrosion behavior of nickel-free Zircaloy-2 and Zircaloy-4 at temperatures up to and including 750 F are shown in Figures 17 and 18, where kinetics very similar to Zircaloy-2 are noted. Figures 19, 20, and 21 show the corrosion properties at temperatures up to 750 F of the three alloys after heat treatment in the beta region (~1900 F) and rapidly cooled. All three alloys show similar corrosion kinetics in water and in 750 F steam when the materials are in the all alpha or beta-quenched condition. The nickel-free alloys, like Zircaloy-2, however, do show a marked dependence of corrosion resistance in steam at 750 F and above upon treatments in the two-phase alpha-plus-beta region. Figure 22 summarizes the data which show that cooling rates in excess of 180 F per minute after heating in the beta region are required to maintain good corrosion properties in 750 F steam.

The corrosion behavior of the alloys in steam at temperatures greater than 750 F is markedly similar to the behavior of Zircaloy-2 in that only the beta-quenched material exhibits good properties. Figure 23 illustrates the differences in the behaviors of the three alloys after 14 days in 950 F - 1500 psi steam. All specimens were tested in the alpha-rolled condition. The Zircaloy-2 specimens shown on the left arm of the fixture at the right have adherent oxides. The Zircaloy-4 specimens, on the right arm of the fixture, have corroded and are spalling. All nickel-free specimens completely disintegrated.

The poor corrosion resistance of nickel-free Zircaloy-2 at elevated temperatures in steam is not surprising in light of previous work which showed that iron, nickel, and chromium, singly or in combination, enhance steam corrosion resistance. Thus, it was anticipated that the removal of nickel would result in decreased high temperature steam corrosion resistance. Furthermore, it was also anticipated that the substitution of additional iron to compensate for the volume of inter-metallic phases reduced by the removal of nickel would restore high temperature

FIG. 1-17. CORROSION OF NICKEL-FREE ZIRCALLOY-2

FIG. 1-18. CORROSION OF ZIRCALLOY-4

FIG. 1-19. CORROSION OF BETA QUENCHED NICKEL-FREE ZIRCALOY-2

FIG. 1-20. CORROSION OF BETA QUENCHED ZIRCALOY - 4

FIG. 1-21. CORROSION OF BETA QUENCHED ZIRCALOY - 2

FIG. 1-22. EFFECT OF COOLING RATE ON 750°F STEAM
CORROSION OF ZIRCALOY - 4

FIG. 1-23. PHOTOGRAPH OF ZIRCALOYS BEFORE AND AFTER CORROSION
IN 950 F STEAM

corrosion resistance. These predictions were verified in 800 and 850 F steam tests where nickel-free Zircaloy-2 samples completely disintegrated within short periods of time, while Zircaloys-2 and -4 showed similar corrosion properties.

Since the incentive for the modification of the Zircaloy-2 composition by minimizing the nickel content was to reduce the tendency for the alloy to absorb hydrogen during aqueous corrosion exposure, extensive work has been performed to evaluate this property. The hydrogen absorption characteristics of zirconium alloys is generally expressed in terms of percent theoretical hydrogen. Percent theoretical hydrogen is an expression which relates the amount of hydrogen picked up by the specimens as a function of the amount of hydrogen liberated by the reaction:

This expression facilitates the comparison between samples of different corrosion resistances and different dimensions; however, it does suffer from a few drawbacks. Table III demonstrates the marked superiority in the hydrogen absorption characteristics of the new materials over Zircaloy-2. Nickel-free Zircaloy-2 consistently picks up less hydrogen in both water and steam than Zircaloy-2, while Zircaloy-4 shows lower hydrogen absorption only in water. These data, however, represent average behavior of the alloys. In many tests with all three Zircaloys, the percent theoretical value was initially low, but upon prolonged exposure increased; in other tests, the value was initially high and remained at that level.

TABLE III - Comparison of Percent Theoretical Hydrogen

	<u>Nickel-Free</u> <u>Zircaloy-2</u>		<u>Zircaloy-4</u>		<u>Zircaloy-2</u>	
	<u>680 F</u>	<u>750 F</u>	<u>680 F</u>	<u>750 F</u>	<u>680 F</u>	<u>750 F</u>
Avg. % Theoretical	12	18	18	28	39	26
Range, High	4	10	10	22	17	17
Low	17	25	26	34	47	47
No. Ingots	9	9	8	8	8	8

Subsequent work with Zircaloy-2 demonstrated that the hydrogen uptake performance can be appreciably altered by fabrication techniques and/or thermal treatment. The results summarized in Figure 24 show that material fabricated at 1450 F initially absorbs small quantities of hydrogen in 750 F steam, but after a period of time, the quantity absorbed increases. Material fabricated at 1550 F (alpha + beta phase fabrication), on the other hand, does not show significant increases in the absorption rate. Initially, the 1450 F fabricated material shows a lower amount of absorbed hydrogen, but at 56 days both materials show like amounts. After 56 days the 1550 F fabricated material repeatedly shows lower hydrogen absorption values. The same general trends are observed in 680 F water, except that the "crossover" point did not occur until after 220 days exposure.

In light of the above information, all prior Zircaloy-hydrogen information was reviewed and was correlated with prior fabrication history or with prior heat treatment. The results of this work are summarized in Figures 25 and 26. In Figure 24 the ratio of hydrogen pickup to the oxygen pickup by nickel-free Zircaloy-2 is plotted as a function of oxygen weight gain. Several items become apparent.

1. A greater quantity of hydrogen per unit of oxygen weight gain is absorbed in steam than in water; although at low weight gains, the hydrogen pickup in 750 F steam by beta-quenched, nickel-free Zircaloy-2 is lowest.
2. Only the material fabricated or heat treated in the two-phase region shows essentially a constant $\Delta H/\Delta O$ ratio. (The $\Delta H/\Delta O$ ratio x 800 is the percent theoretical value.) All other heat treatments produce increasing ratios.
3. In 680 F water and in 750 F steam alpha-annealed material absorbs greatest amount of hydrogen, while the beta-quenched material absorbs the

FIG. 1-24. AVERAGE EFFECT OF FABRICATION TEMPERATURE ON
PERCENT THEORETICAL HYDROGEN
STRIP COUPONS

FIG. 1-25. NICKEL FREE ZIRCALOY-2
(LOW IRON ZIRCALOY-4)

FIG. 1-26. ZIRCALOY-2

medium to least amount of hydrogen.

A similar curve for the hydrogen absorption exhibited by Zircaloy-4 is not complete because of the lengthy times required to obtain high weight gain in 680 F water. However, the 750 F steam curves are in agreement with those presented for nickel-free Zircaloy-2, except that the ratios range between 0.045 and 0.055 (36 to 44% theoretical) for Zircaloy-4 at 160 mg/dm² oxygen gain, while the nickel-free Zircaloy-2 range between 0.038 and 0.046 (30 to 37% theoretical).

Figure 26 contains a similar presentation of the hydrogen pickup performance of Zircaloy-2. Marked differences are readily apparent.

1. A greater amount of hydrogen is absorbed in 680 F water than in 750 F - 1500 psi steam.
2. All heat treatments produce increasing $\Delta H/\Delta O$ ratios with increasing oxygen pickup.
3. The order of magnitude of the $\Delta H/\Delta O$ ratio is much greater for Zircaloy-2 than was previously noted for the non-nickel bearing materials.

The re-evaluation of the Zircaloy-2 composition with respect to the nickel content has produced two alloys which exhibit markedly lower hydrogen absorption values and rates than does Zircaloy-2, and both alloys show aqueous corrosion resistances comparable to Zircaloy-2. Additional evidence that the modification of Zircaloy-2 to that of Zircaloy-4 was obtained during an in-pile experiment. PWR Core 1 type fuel rods were fabricated with both Zircaloy-2 and Zircaloy-4 cladding. Samples with intentional defects in the cladding were irradiated at a surface heat flux of 500,000 BTU/hr-ft². The Zircaloy-2 rod failed because of hydride embrittlement in 3 $\frac{1}{4}$ days; the Zircaloy-4 rod did not fail after about 40 days exposure.

The preceding data clearly indicate that for reactor components exposed to water up to temperatures of 680 F, nickel-free Zircaloy-2 and Zircaloy-4 are

superior to Zircaloy-2 because of lower hydrogen pickup and decreased sensitivity to hydride failure. Zircaloy-4 may be applicable for use at temperatures as high as 825 F; however, Zircaloy-2 is preferred at higher temperatures. If beta treatments are to be employed, all three alloys may be used at temperatures as high as 850 F with preferences given to the non-nickel-bearing materials.

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THE DEVELOPMENT OF ZIRCONIUM ALLOYS FOR PRESSURE TUBES
IN WATER-COOLED POWER REACTORS

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THE DEVELOPMENT OF ZIRCONIUM ALLOYS FOR PRESSURE TUBES
IN WATER-COOLED POWER REACTORS

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INTRODUCTION

The prospect of containing the primary coolant in pressure tubes in a natural uranium water-cooled power reactor is attractive because it offers certain advantages over the pressure vessel concept. The principle advantage is that there is no obvious limit to the size of the reactor and the technology which is developed for the fabrication of pressure tubes is applicable regardless of reactor size. For large reactors the fabrication of pressure vessels presents a formidable technical problem. The disadvantage lies in introducing parasitic material into the core.

The development of Zircaloy-2 in the early 1950's made possible the use of pressure tubes in water-cooled power reactors. Previously, there had not been a material available with the combined properties of adequate low neutron capture cross section, corrosion resistance in high temperature water and strength at temperatures of about 300°C (572°F).

The pressure tubes now in use are fabricated from the Zircaloys. There is still considerable economic incentive to reduce the amount of zirconium alloy in the reactor core to improve both the capital costs and neutron economy. The purpose of this paper is to sketch the history of pressure tube development, show that the Zircaloys in this application have reached the limit of their capabilities and to indicate the investigations that are being carried out to develop stronger zirconium alloys to replace Zircaloy.

HISTORICAL OUTLINE

The development of Zircaloy pressure tubes from ones which operated at maximum allowable stresses of 7500 psi to ones operating at 16,000 psi was not due so much to a change in the material as to a growing

amount of information on its behaviour which gave increasing confidence in its use.

It would be pertinent to sketch the history of pressure tubes with their associated design stresses, because it indicates the growth of knowledge on the properties of Zircaloy-2. Table 1 lists the pressure tube reactors which are built, under construction or being planned.

Table 1
Pressure Tube Reactors

Reactor	Critical	Pressure Tube Materials	Design Stress psi	Temp °C
PRTR	1960	Zircaloy-2	14,400	260
NPD	1962	Zircaloy-2	13,500	300
CANDU	1964	Zircaloy-2	16,000	300
NPR	1963	Zircaloy-2		
SGHWR		Zirconium alloy		
CVTR	1962	Zircaloy-4	18,000	121

The first pressure tube to operate in a reactor core was the loop test section in the central thimble of NRX (1), installed in 1957. The tube was designed to the ASME criterion of 1/4 of the ultimate tensile strength and the maximum allowable stress was 7500 psi at 343°C (650°F). The tube has now operated for about 2000 days or 5-1/2 years at reactor power without incident. It is expected that it will be removed for destructive examination within the next year and be replaced by a new zirconium alloy tube operating at considerably higher stresses.

When a design study for the NPD (Nuclear Power Demonstration) reactor was completed in 1955, it was recommended that it be built with a pressure vessel because insufficient information was available on Zircaloy-2, i.e. effects of irradiation, corrosion resistance, long term creep properties, to recommend it as a material for pressure tubes. By 1957, however, sufficient data were available to redesign NPD to a pressure tube type (2). It was argued that a maximum allowable stress of 1/4 the ultimate tensile strength of annealed Zircaloy-2 was too restrictive and did not exploit the full potential of the material. It was proposed therefore that cold-worked tubes be used and that 1/3 of the ultimate tensile strength would be reason-

able because of the simplicity of the pressure vessel, because of the careful quality control that went into the production of the alloy and because of the stringent inspection of the finished product. This led to a maximum allowable design stress of 13,500 psi (3). The use of cold worked material in a neutron flux raised fears about the effect of neutron damage on the mechanical properties of a metastable metal. Irradiation tests however showed that a reduction in properties did not occur (4) and that radiation hardening was taking place at a faster rate than the annealing at 300°C.

Tensile tests on the NPD tubes showed that the ultimate tensile strength at 300°C lay within the range of 48,000 to 56,000 psi, considerably higher than the values obtained on sheet specimens which were the basis of the design stress. Furthermore it has been shown by several investigators that the bursting hoop stress for tubes is always about 15% higher than the ultimate tensile strength obtained on specimens machined from the tube. The large power reactor now under construction at Douglas Point, Ontario will use Zircaloy-2 pressure tubes at a maximum design stress of 16,000 psi at 300°C (572°F) (5).

For the PRTR (Plutonium Recycling Test Reactor) at Hanford which uses vertical Zircaloy-2 pressure tubes a maximum design stress of 14,400 psi at 260°C (500°F) was chosen (6). The NPR (New Production Reactor) now under construction at Hanford also uses Zircaloy-2 pressure tubes but in a horizontal attitude.

The CVTR (Carolinas-Virginia Test Reactor) uses internally insulated Zircaloy-4 pressure tubes which operate at a maximum design stress of 18,000 psi at 250°F (121°C) (7).

The SGHWR (Steam Generating Heavy Water Reactor) under serious consideration by the U.K. Atomic Energy Authority will probably use zirconium alloy pressure tubes. If Zircaloy is specified then the design stress will be 16,000 psi at 300°C (572°F) (8). Thought is also being given to the use of stronger Zr-Nb alloys so that higher design stresses may be applied.

Mention should also be made of the EL-4 reactor being built by France. This is a heavy water moderated reactor in which the coolant is CO₂. The pressure tubes are Zircaloy-2 which are internally insulated so that they operate at the temperature of the moderator at about 80°C.

From the data now available on Zircaloy it is possible to calculate design stresses over a wide temperature range. Figure 1 shows design stress plotted against temperature for annealed Zircaloy-2. It can be

FIG. 2-1. WORKING STRESS AS DERIVED FROM PRESSURE VESSEL CODE REQUIREMENTS FOR ANNEALED ZIRCALOY-2.

seen that at temperatures above about 400°C the creep becomes the governing criterion and falls off rapidly with rising temperature. Some improvement is possible with cold-worked Zircaloy-2 for which a similar curve is given in Figure 2, in addition to curves for other zirconium alloys. It is clear that the limit of design stress for Zircaloy is about 18,000 psi at 300°C and about 8000 psi at 400°C.

NEW ALLOYS

Since the rewards for reducing the amount of zirconium alloy in the core of a reactor are great both for capital costs and for neutron economy, development work has been stimulated on new zirconium alloys with higher strengths than the Zircaloys.

Studies have been reported on zirconium alloys elsewhere by Douglass (13), Cox et al (14) and investigations are in progress at Oak Ridge National Laboratories, Vallecitos, Armour Research Foundation in the United States, Harwell and Culcheth in the United Kingdom and Metallgesellschaft in West Germany. Detailed reference will be made here to the program in progress at AECL, not because it is the most important but because it is the one most familiar to the author.

At the 1958 Geneva Conference the Russians published results on Zr-Nb alloys which indicated that they might have a suitable alloy to replace Zircaloy-2 in water-cooled power reactors. A program was begun at AECL in 1959 to investigate these alloys and on the basis of the Russian results, a 2.5 wt % Nb alloy was chosen as representing the optimum combination of properties. Indications were that the corrosion resistance of the alloy would not be as high as Zircaloy-2. It must be remembered, however, that the corrosion rate of Zircaloy-2 is extremely low and that the rate of penetration in 30 years is about 0.001 inch. An increase of two or three times this rate would still be quite acceptable.

Even the binary alloy is complex because it is heat-treatable and the heat treatment has an effect on the mechanical properties and the corrosion resistance. The corrosion properties formed a major part of the program and studies were made on a number of melts. The results have been reported by Dalgaard (9). These can be summarized as follows:

1. Sponge base alloy has corrosion resistance as good as the crystal bar base alloy.
2. The corrosion rate of the Zr-2.5 wt % Nb in 300°C water is about two to three times greater than that of Zircaloy-2.

FIG. 2-2. DESIGN STRESSES FOR ZIRCONIUM ALLOYS

3. Additions of Sn, or Fe and Cr, had no significant effect on corrosion resistance but additions of Cu improved the corrosion resistance at higher temperatures.
4. Heat treatment does have a significant effect on corrosion resistance.

The pressure tube in a reactor will see primary coolant on one side and insulating gas on the other. For this reason the corrosion rates were investigated in both air and CO₂. The corrosion rate in air at 300°C is unacceptable. Early results on the corrosion in moist CO₂ at 300°C have indicated that a straight Zr-2.5 wt % Nb alloy may not be acceptable (2.3 mdd) and that a copper addition may be necessary. These early results are suspect, however, and the actual rate for the binary alloy may be considerably lower.

Experiments have been carried out to determine corrosion and hydriding rates under irradiation. Results from recent loop experiments indicate that irradiation in a flux of about $3 \text{ to } 6 \times 10^{13} \text{ n/cm}^2/\text{sec}$ for about 56 days in a steam cooled loop where temperatures ranged from 316°C to 430°C had little effect on corrosion or hydriding rates (10). For this short period of exposure, however, it is difficult to draw conclusions because the specimens will not have passed transition, and a very large change of corrosion rate is necessary in the pretransition stage to be observable.

Heat treatment is required to develop maximum tensile properties of the alloy. The strength of the alloy can be improved by about 50% over that of cold-worked Zircaloy-2 while still retaining considerable ductility (11). The effect of neutron irradiation on both impact and tensile properties of the heat treated alloy have been measured. The most recent irradiations have been in a high temperature water loop of the NRU reactor to a total flux of 10^{21} n/cm^2 ($E > 500 \text{ eV}$) at a temperature of 290°C. Tensile results are given in Table 2. All these specimens were water quenched from 880°C and tempered at 500°C for 24 hours. Even at room temperature with a hydrogen concentration of 250 ppm there is still ductility remaining after irradiation.

It has been found that neutron irradiation has little effect on impact strength at least up to total doses of about 10^{20} n/cm^2 (12).

Creep tests (11) of up to 2000 hours at stresses between 30,000 and 80,000 psi and temperatures between 300°C and 500°C indicate that the creep strength of Zr-Nb is considerably better than that of Zircaloy-2. Longer term tests of up to 10,000 hours are being started.

Table 2

The Effect of Neutron Irradiation on the Tensile Properties of
Hydrided Zr-2.5% Nb

Test Temp (°C)	Hydrogen (ppm)	Prop Limit (kpsi)	0.2% Yield (kpsi)	U T S (kpsi)	% Elongation	% R of A
RT	0	149	161	165	7.5	44
"	13	146	160	163	7.2	43
"	100	140	158	160	5.3	30
"	250	151	163	165	2.5	10
300	0	102	114	118	9.5	65
"	13	109	119	121	8.7	66
"	100	110	117	119	7.5	53
"	250	109	117	119	5.5	33

Temperature of irradiation - 290°C

Total flux 10^{21} n/cm² (E > 500 eV)

It has been the general feeling that the limitation in the life of any zirconium alloy component will be embrittlement due to the precipitation of hydride. This means that the solubility limit must be exceeded and whereas for Zircaloy-2 the solid solubility at 300°C is 100 ppm, for Zr-2.5 Nb at the same temperature it is 180 ppm. Even though the corrosion rate of Zr-Nb is higher than for Zircaloy-2, the hydrogen pickup rate is about the same and therefore the reactor life as determined by the appearance of zirconium hydride should be longer for Zr-Nb than for Zircaloy-2.

There have been to date no difficulties in the fabrication of the Zr-Nb alloys. Pressure tubes and sheathing have both been produced. The most difficult part of the procedure is the heat treatment. Solution treatment is carried out at 880°C followed by a rapid quench. Manufacturers do not recommend salt baths for the solution treatment of long tubes and suitable furnaces are being investigated.

About 65 feet of pressure tubing has been produced, heat treated and tested. The tubes have been subjected to pressure, burst and tensile tests, the results of which have shown satisfactory response to heat treatment. It is proposed to install a Zr-2.5 wt % Nb pressure tube in a pressurized water loop in NRX within the next year with a design stress of 20,000 psi at 300°C.

Indications are that new alloys of zirconium with better properties than Zircaloy-2 are feasible and should appear within the next few years.

DUPLEX TUBES

Another approach to the problem of operating pressure tubes at high design stresses is to select a zirconium alloy on the basis of its mechanical properties without regard for its corrosion resistance and coat it with an alloy such as Zircaloy-2 which has the required corrosion resistance. Wagner et al of A.I. (15) have developed a number of high strength alloys which could be applied to this type of pressure tube. Pressure tubing has been extruded from a Zr-3 wt % Al-0.5 wt % Mo alloy (16) with some difficulty, but it appears possible to select an alloy with better extrusion characteristics.

The most direct method of coating the tube would be to coextrude. Some difficulties might be encountered due to the different extrusion characteristics of the high strength alloy and Zircaloy. Another method which has not been investigated is spray coating.

Any method of fabricating duplex tubes should produce a metallurgical bond between the high strength alloy and the coating because of hydriding considerations. Without a bond, hydrogen may accumulate in the coating and because it is thin, render it brittle in a short time.

Although the duplex tube concept has not been investigated very thoroughly, it offers the promise of a tube with strength in the range of 80,000 to 100,000 psi at 300°C.

FUTURE PRESSURE TUBES

One aspect of pressure tubes which has not been discussed is their design. The tube which operates at the temperature of the coolant, the hot stress tube, surrounded by an insulating gas blanket, offers the simplest technological problems but makes the greatest demands on the material. The cold stress tube which is insulated from the primary coolant does not make as great demands on the material; the problems of fabricating the assembly so that it will withstand thermal cycling is a difficult one. In spite of this it is likely that this is the direction pressure tube design will take in the future because it is the only way in which the temperature of the primary coolant can be raised to temperatures above 350 - 400°C. Although it may be possible to provide corrosion resistant alloys at these tempera-

tures it may not be possible to combine satisfactory strength and creep resistance.

For the hot stress tube it is not possible for Zircaloy-2 to operate at a design stress of more than 18,000 psi at 300°C and it is necessary to develop stronger alloys.

Stronger alloys are available which show that design stresses of about 25,000 psi at 300°C should be possible.

CONCLUSIONS

1. A hot stress tube operating at a design stress of 25,000 psi at 300°C appears feasible.
2. As coolant temperatures increase above 350 - 400°C it will be necessary to adopt a cold stress tube design.

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AN INVESTIGATION OF ZIRCONIUM ALLOYS
FOR RESISTANCE TO CARBON DIOXIDE CORROSION

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ABSTRACT

The investigation had as its objective the selection and/or development of zirconium base alloys suitable for reactor core hardware in a CO₂-cooled, D₂O-moderated reactor. Commercially available alloys were investigated for times to 18,000 hours at temperatures from 800 to 1300°F. Sixty-five experimentally prepared binary alloys containing 26 addition elements at different contents were also investigated. In combination with the limited literature information, most of the elements of possible interest for this application have now been investigated at certain compositions. The data is presented in condensed form and emphasis has been placed on aspects of interest to the general problem of zirconium corrosion.

Multiple rate transition behavior was found at 1050°F, while at 1150°F and above rates were linear. The "order of merit" of the alloys containing various addition elements varied from temperature to temperature. Thermal cycling at times to 3000 hours had little effect on the more resistant alloys as did changes in pressure from atmospheric to 500 psi. Diffusion of oxygen into the metal was not found. Beta heat treatment improved the corrosion resistance of certain alloys. Both similarities and differences in behavior of the alloys in CO₂ as compared with behavior in oxygen were found.

Rather high but acceptable corrosion rates at 1050°F for two year periods were determined for the commercial 1/2% Cu - 1/2% Mo alloys and several of the experimental binary alloys in the dry (<10 ppm H₂O), carbon monoxide free, CO₂ employed. At 1150°F, exposures of several thousand hours were possible without excessive attack. Twelve beneficial alloying elements were identified. Four elements were shown to be deleterious in the compositions tested.

SUMMARY

The Commercial Alloys

The 1/2 Cu, 1/2 Mo alloys have been tested to 18,000 hours at 1050°F in 500 psi, dry CO₂. While attack was moderately heavy, the limit of operation was not reached. At 5500 hours at 1150°F attack was heavy. 17,000 hours at 800°F indicated practically unlimited life at the lower temperature. Slight differences in behavior are apparent in these Cu-Mo alloys as supplied by different manufacturers. The 1 Cu, 1 Mo alloy is slightly inferior to the lower content alloy. "Breakaway" phenomena have not been encountered with these alloys.

The Effect of Variables

Pressure changes from atmospheric to 500 psi have little effect on resistant alloys but tend to markedly increase the rate of corrosion of inferior alloys.

Reasonably severe thermal cycling (915 cycles in 3000 hours) does not affect the corrosion behavior of a resistant alloy in this time span.

High moisture contents (1000 or 100 ppm water as compared with 10 ppm) increased the total weight gains of the alloys tested and the amount of hydrogen absorbed also increased.

Microhardness traverses indicated little diffusion of oxygen into the base metal at long exposure times.

The Binary Alloys

Twelve elements were found to improve the corrosion characteristics of zirconium when alloyed with it. Four elements were found to have definitely deleterious effects. Most of the possible alloying elements for nuclear applications have now been investigated in binary systems.

Heat treatment in the beta region was found to improve the corrosion resistance of several of the binary alloys. Heat treatment should be considered as an important technique for developing CO₂ resistant alloys.

In general the alloys studied gained weight in corrosion through a series of rate transitions rather than by following a simple law.

The quality of a given alloy in comparison with other alloys was found to vary considerably from temperature to temperature at the six test temperatures so that the best alloy at one temperature might be inferior at others.

INTRODUCTION

The work described was initiated as part of a program for the development of a CO₂-cooled, D₂O-moderated, pressure tube reactor, but corrosion resistant, low cross-section alloys are of vital importance to any gas-cooled reactor system. The carbon dioxide cooled reactor program in Great Britain has resulted in the development of the commercially available 1/2% Cu - 1/2% Mo zirconium alloys. Such alloys are, or will be, employed in reactor core components in at least six of the British Magnox reactors.¹

The program described was intended to determine the exposure lifetimes and other characteristics of the commercial Cu - Mo alloys under the special conditions expected in a D₂O-moderated reactor. These conditions included a carbon monoxide free gas and operating temperatures in the 1050°F range. A second important aspect of the work was the preliminary investigation of binary alloys containing as yet unreported addition elements. The objective here was to round-out the rather limited literature data to provide at least a minimum of information on all the elements of interest, so as to have available basic data for the development of improved alloys.

Five commercial alloys and some 65 experimental binary alloys containing 26 addition elements in various percentages were investigated. Tests were carried out at 800, 950, 1050, 1100, 1150 and 1300°F. The data is, however, presented in condensed form and those phenomena, such as the multiple rate transition weight gain behavior, which may be of interest to other zirconium alloys corrosion problems, have been emphasized.

EXPERIMENTAL TECHNIQUES

The experimental corrosion exposures were carried out under static conditions in a continuously replenished atmosphere. Specimens were supported by stainless steel wire grids in Inconel boats within horizontal Inconel autoclaves in well insulated furnaces. The flow of carbon dioxide through the autoclaves was approximately 1/4 cu ft per hour. The carbon dioxide used was a standard commercial product with the following analysis:

CO₂ -- 99.9% by weight*

CO -- trace to 0.052% by volume

O₂ -- trace to 0.004% by volume

N₂ -- 0.012 to 0.035% by volume

H₂O -- 0.005 to 0.008% by volume

SO₂ -- 0.000% by weight*

Oil -- 0.001% by weight*

H₂S -- 0.000% by weight*

No carbon monoxide or other gas was added to the carbon dioxide in these experiments. The specimens were approximately 1 x 1/2 x 0.5 in. in size. Their edges were broken, but not rounded, a matter of importance as most of the protective oxide films tend to crack at sharp corners.

CO, O₂ and N₂ contents of the gas were continuously monitored with a Beckman Industrial Chromatograph. Moisture contents were determined with an electrolytic hygrometer - the Consolidated Electrodynamics Corporation Moisture Monitor. Before entering the loops the carbon dioxide was dried to below 10 ppm water by passage through a column containing Linde 5A molecular sieve packing. This packing also appears to remove all the oil usually present in commercial CO₂.

Proportional input controllers maintained the furnace temperatures. The temperature recorders used were stated to have an accuracy of + 4°F and are believed to have operated within this limit. An automatic alarm system on the recorder was set to shut off any furnace whose temperature rose to 7°F above the set point. Considerable effort was devoted to temperature measurement and control. Routine checks were made of all the instruments against a Rubicon potentiometer with a Pt-Rd thermocouple. The chromel-alumel thermocouples were changed at 1,000-hour intervals. While

* Manufacturer's specification - other figures are operating data determined on the GNEC gas chromatograph and Moisture Monitor.

no difficulty has been encountered with these couples at GNEC, deterioration of chromel-alumel under these conditions has been reported elsewhere. Temperature profiles through the autoclave hot zones were determined and all specimens were placed within an area having a maximum deviation of ± 0 , -7°F from the set temperature. After 2 years of operation, the temperature control in the furnaces was as follows:

Time at set temperature, $\pm 0 - 5^{\circ}\text{F}$ - minimum 93% of time

Time at set temperature, $\pm 0 - 10^{\circ}\text{F}$ - minimum 97% of time

Time at set temperature, $\pm 5 - 10^{\circ}\text{F}$ - minimum 99% of time

Time at more than 7°F above set temperature - 0

The control and measurement of moisture contents in the carbon dioxide required considerable care. The electrolytic hygrometer gave reliable operation, but it was necessary to calibrate it against dew points obtained by conventional methods. To obtain calibrations in the 10 ppm range, dew points had to be determined down to -80°F , a cumbersome and time-consuming operation. However, enough dew point determinations were made to assure confidence in the electrolytic hygrometer. At 10 ppm moisture contents, experimental difficulties are encountered in drying out metal gas lines. Several days may be required to remove all the moisture from the inside of a few feet of copper tubing by passing gas through it. Rubber tubing cannot be used even for short connections because of its surprisingly high permeability to moisture.

The CO_2 Dissociation Experiment

The gas chromatograph was particularly valuable for determining effluent gas purity during the purging operation before starting an experiment. It was also used in a special experiment to determine the temperature at which the $\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$ decomposition becomes appreciable in the presence of zirconium metal. In this experiment commercially pure zirconium chips were heated in a Vycor tube and the CO in the effluent determined with the chromatograph. The sensitivity of the instrument was believed to be not greater than 0.01% by volume. CO measurements were made at 100°F increments on heating, and it was necessary to hold at each temperature for 30 minutes to an hour to secure an accurate CO determination. In the first test the surface of the zirconium chips was abraded with emery paper; in the second, a conventional pickling solution (97.5 ml HNO_3 , 5 ml HF , 100 ml H_2O) was used to etch the metal surface.

Heat Treatments

These were all carried out in the beta region. Standard size specimens were held at 1750°F for one hour in an atmosphere of "gettered" argon. The beta quenched specimens were quickly dropped into water from this temperature. A maximum of 15 seconds was required for the specimens to pass

from 1750°F to 80°F. The beta cooled specimens (BHT on figures) were held in a small furnace with the power off. One hour was required to pass from 1750° to 1200°F, and an additional two hours were necessary to reach room temperature. The atmosphere was sufficiently pure so that the specimens showed only a light "heat-tint" coloration on the surface even after quenching. All surfaces were, however, removed on emery paper before testing.

The Thermal Cycle Experiment

This work was done in a small split furnace. Specimens were held in a Vycor tube with flexible inlet and outlet gas connections. The cooling portion of the cycle (25 minutes) merely required that the furnace be opened and the tube lifted out and placed on a holder a few inches away. For the 35-minute heating period, the tube was replaced in the furnace. The daily operation consisted of eight heating-cooling cycles and 16 hours continuously at temperature.

Conventional metallographic techniques have been employed. Penetrations were measured by comparing the thicknesses of unaffected metal in the corroded specimens, as determined with a filar eyepiece on the metalloscope, with the original thickness of the specimen as measured with a micrometer. Microhardness traverse data were obtained from hardnesses measured with an Eberbach Microhardness Tester with a Vickers pyramid diamond indenter. It was not possible to make accurate readings closer than 0.02 mm from the edges as the hard adherent oxide film interfered with the indenter.

MATERIALS INVESTIGATED

The Commercial Alloys

Three groups of materials were investigated. The first consisted of those copper-molybdenum alloys available commercially. The ATR (1/2 Cu, 1/2 Mo) and AJR (1 Cu, 1 Mo) alloys were purchased from Carborundum Metals Company.* Zirconium-30** (1/2 Cu, 1/2 Mo) and Zirconium-10 (reactor-grade pure zirconium) were purchased from Imperial Chemical Industries Ltd., Metals Division. Analytical data for these materials are given on Table 1. Information is included on this table for an experimental alloy produced by Combustion Engineering, Inc.

The Alloys Produced by Reactive Metals, Incorporated

The second group of materials was a set of 35 experimental binary alloys representing 12 addition elements produced to GNEC specifications by Reactive Metals, Inc. An analysis of the zirconium metal used in fabricating the alloys is given on Table 2 and the analyzed compositions as well as the nominal compositions of all the alloys produced are given on Table 3. These alloys are referred to by their actual analyses herein.

These RMI alloys were produced² in 5-pound quantities by double melting of a compacted electrode containing the high purity alloying additions. For most of the alloys, the first melting operation was performed under a pressure of argon and the second melting under vacuum. Difficulty was experienced in holding the high-vapor-pressure elements barium, tellurium, and cerium in the melt so that these alloys underwent both melting operations under 15 psig of argon. The double melted ingots were conditioned and forged at 1700-1750°F. Rolling was carried out at 1400-1600°F, except for the beryllium alloys which were hot rolled at 1200°F. Higher rolling temperatures resulted in rippled and unsatisfactory sheet from the beryllium alloys.

A one-hour annealing operation was carried out for the alloys at a temperature 200°F below the beta transus. It was necessary to approximate the beta transus temperature for the yttrium, barium, cerium, tellurium, and palladium alloys experimentally. The material was tested in three conditions, as hot rolled, as annealed and then furnace cooled from the annealing temperature, and as annealed and air cooled.

The Alloys Produced by Armour Research Foundation

The third group of zirconium alloys were made available by Armour Research Foundation which had prepared them originally as part of a program for the development of steam and hot water resistant materials. Many of these alloys contained addition elements in the proper percentages to be of

* Produced under license from Associated Electrical Industries, Ltd.

** Produced under license from Metropolitan Vickers Electrical Company, Ltd.

Table 1 COMPOSITIONS OF THE COMMERCIAL ZIRCONIUM ALLOYS

<u>Nominal Composition</u>	<u>Weight Percent</u>			<u>Parts Per Million</u>									<u>Condition</u>
	<u>Cu</u>	<u>Mo</u>	<u>Sn</u>	<u>Fe</u>	<u>Hf</u>	<u>Cr</u>	<u>Si</u>	<u>Al</u>	<u>Ti</u>	<u>N₂</u>	<u>H₂</u>	<u>Ni</u>	
1/2 Cu, 1/2 Mo (Carborundum ATR)	0.44	0.42		380	140	67	50				6		Hot rolled
1/2 Cu, 1/2 Mo (ICI-Zr-30)	0.50	0.56		600	70	130	50	180					Cold rolled
1 Cu, 1 Mo (Carborundum AJR)	0.91	0.90		440	140	107	50						Hot rolled
Pure zirconium (ICI-Zr-10)				1200	50			65	15	35	7		Cold rolled
Zircaloy-2 (RMI)			1.39	1227	45	793	30	33	20	50	19	533	Hot rolled
Tin-Molybdenum*	1.0	0.42	0.20										Hot rolled

* Experimental alloy.

Table 2 COMPLETE CHEMICAL COMPOSITION OF FIVE ZIRCONIUM BINARY ALLOYS
AND THE PURE ZIRCONIUM USED IN THE PREPARATION OF THE
RMI ALLOYS

<u>ELEMENT</u>	<u>PURE Zr</u>	<u>Zr-1Ti</u>	<u>Zr-.5Ti</u>	<u>Zr-.25Cr</u>	<u>Zr-.5Cr</u>	<u>Zr-1Cr</u>
Al, ppm	< 20	26	27	27	27	26
B, ppm	< .3	< .3	< .3	< .3	< .3	< .3
Cd, ppm	< .3	< .3	< .3	< .3	< .3	< .3
Cr, ppm	< 20	< 20	< 20	0.25%	0.54%	1.0%
Co, ppm	< 5	< 5	< 5	5	< 5	< 5
Cu, ppm	10	39	13	10	< 10	20
Hf, ppm	55	--	--	--	--	--
Fe, ppm	235	220	200	200	200	200
Si, ppm	< 30	30	33	30	30	30
Ti, ppm	25	0.79%	0.52%	74	35	20
Pb, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Mn, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Ni, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Na, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Mg, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Mo, ppm	< 20	< 20	< 20	< 20	< 20	< 20
Sn, ppm	< 20	< 20	< 20	< 20	< 20	< 20
V, ppm	< 20	< 20	< 20	< 20	< 20	< 20
C, %	91	--	--	--	--	--
O, %	0.084	--	--	--	--	0.073%
N, ppm	26	--	--	--	--	36
H, ppm	14	--	--	--	--	17

Table 3 CHEMICAL ANALYSES OF THE BINARY ZIRCONIUM BASE
ALLOYS PREPARED BY REACTIVE METALS, INC.

NOMINAL COMPOSITION	ANALYZED COMPOSITION %	OXYGEN, ppm	HYDROGEN, ppm	NITROGEN, ppm	CHLORINE, ppm	BHN 1500 kg, LOAD	
						TOP	BOTTOM
Zr, pure	----	840	14	26	--	128	127
Zr-1Ti	0.79	960	14	26	--	158	157
Zr-.5Ti	0.52	---	--	--	--	155	162
Zr-1Cr	1.0	730	17	36	--	183	176
Zr-.5Cr	0.54	---	--	--	--	182	174
Zr-.25Cr	0.25	---	--	--	--	165	---(1)
Zr-1Be	1.03	---	--	--	--	175	157
Zr-.5Be	0.48	---	--	--	--	136	145
Zr-.25Be	0.20	---	--	--	--	136	128
Zr-2Y	1.75	750	49	38	--	125	---(1)
Zr-1Y	0.80	---	--	--	--	149	147
Zr-.5Y	0.45	---	--	--	62	136	113
Zr-15Cb	17.0	950	39	63	--	201	206
Zr-2Cb	1.9	660	10	--	--	167	169
Zr-1Cb	0.88	---	--	--	--	146	145
Zr-.5Cb	0.44	---	--	--	--	145	150
Zr-1Ag	1.35	832	86	32	78	155	152
Zr-.5Ag	0.71	---	--	--	--	145	147
Zr-.1Ag	0.25	---	--	--	--	135	136
Zr-2V	2.2	640	13	--	--	186	199
Zr-.5V	0.56	---	--	--	--	154	158
Zr-.25V	0.27	---	--	--	--	138	146
Zr-1Mn	.32	750	56	--	--	142	147
Zr-.5Mn	.38	---	--	--	--	150	144
Zr-.1Mn	.11	---	--	--	--	135	137
Zr-.1Pd	.120	760	18	--	--	133	137
Zr-.02Pd	.033	---	--	--	--	138	136
Zr-.5Ba	.010	---	--	--	--	141	139
Zr-.1Ba	.010	---	--	--	--	125	129
Zr-1Te	1.06	870	24	--	--	144	160
Zr-.5Te	.70	---	--	--	--	141	139
Zr-.1Te	.18	---	--	--	--	137	127
Zr-1Ce	0.4	---	--	--	--	137	136
Zr-.5Ce	.13	---	--	--	--	149	149
Zr-.1Ce	.04	---	--	--	--	142	131

(1) Porous bottom; no reading taken.

special interest to the GNEC program. The alloys of the third group are listed on Table 4.

As analytical data are available only for a few of the ARF alloys, all these alloys are referred to by their nominal compositions in this paper. These alloys were prepared in laboratory (100 gm) quantities by non-consumable arc melting under a positive argon pressure.³ As contrasted with the RMI procedure in which the alloys were hot rolled bare, the Armour alloys were canned in steel for rolling. The reduction process consisted of annealing at 1550 for one hour, rolling, re-annealing, and rolling again at this same temperature. Final rolling was done at 1350°F. This was followed by annealing at 1350°F and air cooling in the steel clad. Specimens were machined at GNEC from their original thickness of 80 to 95 mils to 50 mils to remove possible contamination from the steel clad. As these specimens were received late in the program, time was not available for the long test exposures reported for the commercial and RMI alloys.

All the addition elements investigated in this program are listed in the first column of Table 5 which also lists elements investigated in other programs. Figure 1, a periodic chart, shows the elements investigated and their group relationships.

Table 4 THE SECOND GROUP OF BINARY ZIRCONIUM ALLOYS
SUPPLIED BY ARMOUR RESEARCH FOUNDATION

<u>Addition Element</u>	<u>Nominal or Intended Content, %</u>	<u>Content as Determined by Analysis, %</u>
1. Gold	.25 1.0	
2. Bismuth	.25	
3. Cobalt	.25 1.0	
4. Copper	.25 1.0 3.0	.25 .96 2.91
5. Iron	.25 1.0	
6. Germanium	.25 1.0	
7. Molybdenum	.25 1.0 3.0	
8. Lead	.25 1.0	.26 .60
9. Rhodium	.25 1.0	
10. Antimony	.25 1.0	
11. Silicon	.25 1.0	
12. Platinum	.25 1.0	
13. Nickel	.25 1.0	.96 2.56
14. Vanadium	3.0 5.0	1.61

Table 5 LIST OF ELEMENTS TESTED AS BINARY ADDITIONS TO ZIRCONIUM

For Resistance to Corrosion by Hot CO ₂		For High Temperature Oxidation Resistance	
This Program	O'Driscoll, et al (4)	Porte, et al (5)	Other
1. Beryllium	Beryllium	Beryllium	
2.	Carbon	Carbon	
3.	Nitrogen		
4.	Oxygen		
5. Aluminum	Aluminum	Aluminum	
6. Silicon	Silicon	Silicon	
7.			Phosphorous (6)
8. Titanium		Titanium	
9. Vanadium	Vanadium	Vanadium	
10. Chromium		Chromium	
11. Manganese			
12. Iron	Iron	Iron	
13. Cobalt		Cobalt	
14. Nickel	Nickel	Nickel	
15. Copper	Copper	Copper	
16. Germanium			
17. Yttrium			
18. Niobium	Niobium	Niobium	
19. Molybdenum	Molybdenum	Molybdenum	
20. Rhodium			
21. Palladium			
22. Gold			
23.	Indium		
24. Silver	Silver		
25. Tin	Tin	Tin	
26. Antimony			
27. Tellurium			Tellurium (7)
28. Barium			
29.	Tantalum	Tantalum	
30.	Tungsten	Tungsten	
31. Platinum		Platinum	
32. Lead		Lead	
33. Bismuth			
34. Cerium			
35.		Hafnium	
36.		Uranium	

PERIODIC TABLE OF THE ELEMENTS

																	1 H																	2 He			
0	I		II		III		IV		V		VI		VII		VIII																						
2 He	3 Li		4 ^{AB} Be		5 B σ		6 ^B C		7 ^B N		8 ^B O		9 F		10 Ne																						
10 Ne	11 Na		12 ^{AB} Mg		13 ^{AB} Al		14 ^{AB} Si		15 [*] P		16 S		17 Cl		18 Ar																						
0	I a	II a	III a	IV a	V a	VI a	VII a	VIII a		I b	II b	III b	IV b	V b	VI b	VII b	VIII b																				
18 Ar	19 K	20 ^A Ca	21 Sc σ	22 ^A Ti	23 ^{AB} V	24 ^A Cr	25 ^A Mn	26 ^{AB} Fe	27 ^A Co σ	28 ^{AB} Ni	29 ^{AB} Cu	30 ^A Zn	31 Ga	32 ^A Ge	33 As	34 Se	35 Br	36 Kr																			
36 Kr	37 Rb	38 ^A Sr	39 ^A Y	40 Zr	41 ^{AB} Nb	42 ^{AB} Mo	43 Tc σ	44 Ru	45 ^A Rh σ	46 ^A Pd	47 ^{AB} Ag σ	48 Cd σ	49 ^B In σ	50 ^{AB} Sn	51 ^A Sb	52 ^{A*} Te	53 I	54 Xe																			
54 Xe	55 Cs	56 ^A Ba	57 ^A La	58 Ce σ	59 Pr σ	60 Nd σ	61 Pm σ	62 Sm σ	63 Eu σ	64 Gd σ	65 Tb σ	66 Dy σ	67 Ho σ	68 Er σ	69 Tm σ	70 Yb σ	71 Lu σ																				
86 Rn	87 Fr	88 Ra σ	89 Ac σ	90 Th	91 Pa	92 U																															
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																			
58 ^A Ce	59 ^A Pr	60 Nd σ	61 Pm σ	62 Sm σ	63 Eu σ	64 Gd σ	65 Tb σ	66 Dy σ	67 Ho σ	68 Er σ	69 Tm σ	70 Yb σ	71 Lu σ	RARE EARTH METALS																							

FIG. 3-1. Periodic chart with the possible alloying elements for this application shown in large letters. Binary alloys of the elements shown in boxes have been investigated. Those underlined have been shown to have beneficial effects. The letter A indicates study in this program. B indicates elements reported in reference 4. See Table 5 for those marked with an asterisk. Encircled elements are of possible interest but have not been investigated. The symbol σ indicates elements of excessive thermal neutron cross-section.

RESULTS

The Effects of Temperature on Corrosion Behavior

The temperatures of interest for possible reactor use were 1150, 1050, and 800°F. 1050°F was assumed to be the most probable bulk gas temperature, and was, therefore, the temperature of greatest interest. In addition to the above temperatures an accelerated test was run at 700°C (1292°F) and some tests were also conducted at 950 and 1100°F to fill in the temperature spectrum. Figure 2 shows low corrosion rates and acceptable behavior for the commercial alloys at 17,000 hours at the comparatively low temperature of 800°F. The curves also clearly show that weight changes do not occur at a constant rate, or at a rate corresponding to a parabolic, cubic, or similar law, but in a series of steps. These steps, or rate transitions, are found for each curve. If the curve defined by the triangular symbol points of Fig. 2 were drawn alone in the conventional manner, a smooth, roughly parabolic, curve would result. The scatter of the points caused by the magnified scale on the ordinate would produce a fairly satisfactory fit of the smooth curve to the points. The rate transitions which actually occurred would be masked by such conventional plotting and, as suggested by Griggs,⁸ the question arises as to whether or not rate transitions are not occasionally concealed by the usual techniques of curve preparation employed in the corrosion literature. The plotting of data on semilogarithmic or, more particularly, on log-log paper, masks these rate transitions.

Data such as that shown in Fig. 2 for the square symbols would be forced into a smooth curve with difficulty because of the unusually small scatter. However, both the square and triangular symbol point curves are nearly identical and would indicate both valid data and a multiple rate transition mechanism of corrosion behavior.

The temperature of greatest interest was 1050°F, and the representative behavior of several alloys at this temperature is shown on Fig. 3. The Zircaloy-2 can be considered as having gone quickly into breakaway - one of the rate instances of this phenomena found. The weight gain behavior of the four binary alloys is reasonably low, and for the 4,000 hours plotted at least, resemble the 1/2 Cu, 1/2 Mo alloy in rate. No rate transitions are apparent in this time.

As the commercial alloys were available at the start of the program, it was possible to obtain the 18,000 hour exposures shown on Fig. 4 for 1050°F. Here, rate transitions are again apparent, particularly in the case of the tin-containing alloy. Although the weight gain rate is excessive for the tin alloy for most of the exposure, the brief operation of some protective mechanism at about 5,000 hours is apparent.

The 1/2 Cu, 1/2 Mo alloy is definitely superior to the 1 Cu, 1 Mo alloy. The total weight gain and rate of weight gain for the 1/2 Cu, 1/2 Mo alloy are high but probably do not make the alloy unusable for many applications.

FIG. 3-2. Weight gain behavior for long-time exposures at 800°F and 500 psi..
Note expanded scale of ordinate.

FIG. 3-3. Behavior of representative alloys after 4000 hours at 1050°F and 500 psi in dry (< 10 ppm water) carbon dioxide.

FIG. 3-4 The behavior of four copper-molybdenum alloys after prolonged exposure at 1050°F and 500 psi pressure in dry CO₂.

1050°F was considered the use temperature for the original program, and the behavior at 18,000 hours is considered acceptable. The increased scatter of the data points is indicative of deterioration but no sign of breakaway is as yet apparent.

A material intended for use at 1050°F could be expected to be occasionally exposed to temperatures 100 degrees higher. Some degree of corrosion resistance at 1150°F was, therefore, important. It was also believed that 1150°F might furnish an accelerated test for 1050°F behavior. The data presented on Fig. 5 is from an 1150°F atmospheric pressure, test of 5,500 hours duration. It is seen that corrosion rates tend to be linear after the first 1,500 hours. Only the barium and the 2.2% vanadium alloys show slightly decreasing rates with time. Pure zirconium was considered to have failed at 2,000 hours. The as-received, hot-rolled Carborundum 1/2 Cu, 1/2 Mo alloy was found to be superior to its heat treated form, and to the similar ICI alloy, at this temperature.

Figures 6A and 6B present shorter term tests of the ARF alloys at 1150°F. The 1% and 0.25% molybdenum alloys seems to show increasing rates at the end of the test and may be entering rate transition periods. The 1% and 3% copper alloys are superior to the 1/2 Cu, 1/2 Mo alloy as plotted, but the long-time data on Fig. 4 for the 1% Cu alloy would suggest the possibility that the superiority of these high copper alloys might not necessarily be maintained for long periods.

Copper to 3%, vanadium to 3% (Fig. 6A), nickel to 1% and other elements show an addition effect in that increased quantities of the alloying element, up to a limiting figure, increase corrosion resistance. Molybdenum showed a reverse phenomena in that increasing quantities of molybdenum decreased corrosion resistance.

The highest temperature experiment carried out was a short time screening test at 700°C (1292°F) in dry CO₂ at atmospheric pressure. Only one weighing was made at the end of 400 hours. Weight gains measured are tabulated in Table 6. For reasons discussed below, this test had limitations as an accelerated test and, from the results obtained, the temperature was obviously too high to represent a possible use temperature. Data is also given on Table 6 for temperatures of 800, 950, 1050, 1100, and 1150°F. The alloys listed are what might be called the "short" list; that is, a group of alloys which were available sufficiently early in the program so that testing at several temperatures was possible. Table 7 gives the order of merit of a longer list of alloys including the ARF alloys, at only the two temperatures, 1050 and 1150°F. On these tables a few selected alloys have been followed from temperature to temperature by interconnecting lines so that changes in the order of merit of the alloys at different temperatures are more apparent. Alloys whose weight gains fell within 2% of each other were given the same order of merit number.

Figures 7 and 8 present weight gain curves for commercially pure zirconium and the 1/2 Cu, 1/2 Mo alloy at the six temperatures. For the

Table 6 ORDER OF MERIT COMPARISONS AT SIX TEMPERATURES

[illegible]

Table 7 ORDER OF MERIT COMPARISONS AT TWO TEMPERATURES

1050°F - 500 psi 2500 hours			1150°F - Ambient 3500 hours		
No.	Alloy	Average Wt. gain mg/dm ²	No.	Alloy	Average Wt. gain mg/dm ²
1	0.25 Si	128	1	3.0 Cu	508
2	3.0 V	229	2	1.0 Cu	722
3	0.25 Sb	237	3	1/2 Cu, 1/2 Mo (Carb.)	802
4	1.0 Pb	284	4	1/2 Cu, 1/2 Mo (Carb.)	1036
5	1/2 Cu, 1/2 Mo (Carb.) 3.0 Cu	290 291	5	0.04 Ce-βQ 0.20 Be-βQ 1/2 Cu, 1/2 Mo (ICI)	1315 1325 1332
6	0.25 Pb 1.0 Pt	293 297	6	0.25 Mo 2.2 V-AC Pure Zr. βQ (RMI)	1377 1388 1394
7	0.25 Pt	305	7	3.0 V 0.32 Mn-FC 0.01 Ba-β	1435 1450 1459
8	1.0 Ni 1.0 Cu	318 322	8	1.0 Ni	1471
9	3.0 Ni 0.25 Cu	361 361	9	0.12 Pd-βQ 0.1 Cr-HR	1556 1571
10	0.25 Ni 0.01 Ba-HR	383 385	10	0.25 Cu 1.0 Pt	1596 1626
11	1.0 Sb 2.2 V-AC	410 414	11	0.25 Ni 1.0 Mo 0.25 Pb	1672 1685 1686
12	0.04 Ce-βQ	423	12	0.25 Rh	1725
13	0.2 Be-βQ Pure Zr. (ICI) βQ	444 448	13	1.0 Au	1917
14	1.0 Si 0.12 Pd-AC	472 475	14	5.0 V 3.0 Mo	1970 2005
15	1.0 Au	514			

Failed at 1150°F

FIG. 3-5 The behavior of representative materials at 1150°F in dry CO₂ at atmospheric pressure. The scatter band represents the results of four separate tests, each of which contained three specimens.

FIG. 3-6A. 3000-hour data for 1150°F, atmospheric pressure, dry carbon dioxide.

FIG. 3-6B. A continuation of Fig. 6A.

FIG. 3-7. The effect of temperature on the weight gain behavior of commercially pure zirconium (ICI) in dry (< 10 ppm water) CO_2 . The tests at 1292°F and 1150°F were at atmospheric pressure and the others at 500 psi.

FIG. 3-8. The weight gain behavior of the 1/2 Cu, 1/2 Mo (Carborundum) alloy at six temperatures in dry CO₂. The tests at 1292°F and 1150°F were at atmospheric pressure, the remainder at 500 psi.

pure zirconium, the behavior shown on Fig. 7 is what might be expected in that corrosion weight gains and rates increase in regular increments with temperature. For the 1/2 Cu, 1/2 Mo alloy (Fig. 8), the behavior is less conventional, the weight gains at 950°F are less than at 800°F, and for the first 3,000 hours the 1100°F curve is very similar to the 1050°F curve. However, beyond 3,000 hours, these curves separate quickly, and a considerable higher rate is found for 1100°F than at 1050°F for the last 1000 hours plotted. The 950-800°F data do appear anomalous, however. There is some inter-penetration of the two scatter bands as shown and testing with a larger number of specimens might indicate a more complete overlay of the two bands so as to make it appear that the 800 and 950°F weight gain behavior is much the same, rather than having the higher temperature show any marked superiority. The experiment conducted on the effect of zirconium metal surfaces on the $\text{CO}_2 \rightarrow \text{CO}$ decomposition may throw some light on this similarity of behavior at the two temperatures. Carbon monoxide measurements in the experiment whose results are shown in Fig. 9 would be affected by the amount of surface area per unit of volume, the rate of gas flow, the chemical impurities in the metal, and the sensitivity of the measuring instrument. The time of exposure of the metal to gas at a given temperature is also important as protective films form rapidly. However, our previous data showed that 100 hours or more are required for the initial linear rate of attack to fall. The above factors qualify possible conclusions from Fig. 9, but it appears safe to say that below a temperature in the 800 to 1000°F region, depending on the surface, carbon dioxide is relatively inert in the presence of zirconium metal. Above this temperature, CO_2 is readily decomposed; the activity increasing exponentially with temperature. The curves show that this temperature is greatly affected by the character of the metal surface, but for the chemically etched surface the activity is so slight that similar behavior at 800 and 950°F is not surprising. The chemically etched surface could be considered as having been "passivated" and is less reactive than the abraded surface. While this effect is marked, it is felt that most similar surface treatments are rather temporary in nature in that, after an adequate thickness of the passivated surface has been oxidized, the remaining metal is on an equal footing with untreated material. For this reason passivation techniques have not been studied in this program as they have been considered of little permanent value for corrosion resistance to 25,000 hours, even though they might still be important at 5,000 hours. However, it can be suggested that unintentional passivation may have had some effect on the experimental results for periods possibly as long as several thousand hours, as in the 950°F results in question. The stability of CO_2 in the 800°F range would indicate low corrosion rates for all zirconium alloys at this temperature - a condition that has been found to hold. Because these low temperature corrosion rates are so low (Figs. 7 and 8), minor matters such as passivation or other factors affecting surface conditions might explain observed differences in behavior.

Data published by Gregg, Hussey and Jepson⁹ are of interest in this connection. In the curve reproduced on Fig. 10, a delay phenomenon is shown for the temperatures 650°C and 550°C. For these curves the weight

FIG. 3-9 The effect of temperature on the $\text{CO}_2 \rightarrow \text{CO}$ reaction for two surface conditions of commercially pure zirconium.

FIG. 3-10. "Oxidation of zirconium at 550, 650 and 750°C in carbon dioxide at 10 cm pressure." Insert at lower left corner reproduced from Reference 9. The dashed curve represents test results in this program for a 1050°F test temperature.

gain is quite small for the first 20-hour period and then rapidly increases after this delay period. The figure is of interest in that it shows the fine structure of corrosion behavior in the first 140-hour period as revealed by the microbalance technique. A curve from the 1050°F data developed in this program has been added. While it is in general agreement with the reference results, the delay or incubation time phenomenon is, of course, not shown. An understanding of the factors which cause this delay time, if they are not inherently temporary in nature, might be of value in developing better alloys; however, passivation would appear to be a plausible explanation, or partial explanation. The continuation of the microbalance experiments to long exposure times, particularly to beyond the 3,000 range where rate transitions have been encountered, would be of interest in revealing the fine structure of this behavior. The authors⁹ also attribute 98% of the total weight gain in carbon dioxide to the reaction,

and the remaining 2% of weight gain to carbon deposition. Breakaway phenomena are then attributed to carbon deposition on the oxide surface and its possible diffusion into the oxide layer.

Weight gain rates are given on Table 8. These rates were calculated from the expression:

$$\text{Rate} = \frac{\text{Unit weight gain at time 2} - \text{Unit weight gain at time 1}}{\text{time 2} - \text{time 1}}$$

which assumes a linear rate. Actually, the rate was truly linear only in the case of the 1150°F data as shown on the figures. However, the times used for the calculation, as given on the table, were selected to provide rates for the "flatter" portions of the weight gain curves.

The Absorption of Hydrogen and Oxygen

The amount of hydrogen absorbed can be expected to limit the useful lifetime of a zirconium alloy in any application.^{10,11} While the amount of hydrogen available to the metal can hardly be controlled when exposed to steam or water, the careful drying of carbon dioxide permits control in this medium. Hydrogen was therefore determined on specimens exposed to dry and wet gas as shown in Table 9.

The double figures, separated by commas, in the Table represent the results of two separate analyses. As would be expected, the amount of hydrogen absorbed is much greater at the same conditions in the higher moisture content gas at 1150°F. But, while the moisture content in one of the tests was 100 times greater, the hydrogen absorbed was only roughly three times greater. There is also a slow absorption of hydrogen even in dry gas at 800°F and 1050°F, but the rate of absorption is roughly twice as great at 1050°F as at 800°F.

Table 8 RATES OF WEIGHT GAIN AT THREE TEMPERATURES

<u>Conditions</u>	<u>Time Span</u>		<u>Rate, mg/dm²/hr</u>	
	<u>T₁</u>	<u>T₂</u>	<u>1/2 Cu, 1/2 Mo (Carb.)</u>	<u>Pure Zr (ICI)</u>
800°F - 500 psi	3000	13000	0.008	0.0067
	2000	9500		
1050°F - 500 psi	2000	15000	0.045	0.225
	1000	7000		
1150°F - atm	1000	7000	0.170	0.667
	1000	3000		

Table 9 THE EFFECT OF EXPOSURE CONDITIONS
ON HYDROGEN CONTENT

	Hydrogen, ppm	
	<u>1/2 Cu, 1/2 Mo (Carborundum)</u>	<u>Pure Zr (ICI)</u>
As received material	6, 6	7, 8
At 1150°F after 2000 hours in 10 ppm CO ₂	9, 9	11, 12
At 1150°F after 2000 hours in 1000 ppm CO ₂	26, 36	32, 34
At 800°F after 12,347 hours in 10 ppm CO ₂	21, 21	
At 1050°F after 15,074 hours in 10 ppm CO ₂	49, 50	

The water content of the carbon dioxide has other important corrosive effects aside from hydrogen absorption. The over-all effect of water content was determined in three experiments at three moisture levels at 1150°F. The results are shown in Fig. 11. With other conditions held constant, the change in moisture content has produced appreciable changes in weight gain for the representative materials plotted. It will be observed that the weight gain for the 1/2 Cu, 1/2 Mo alloy is greater for the 1,000 ppm gas than for 100 and 10 ppm, but that the rate of weight gain remains almost the same for the three experiments, at least for the 2000-hour period investigated. For the other materials the effects of moisture are more marked.

The role of oxygen and its method of diffusion through the oxide layer and into the metal has been the subject of considerable discussion. It is certain, however, that oxygen is highly soluble in metallic zirconium and that it hardens the metal considerably when in solution. It would seem, then, that the microhardness traverse technique should disclose diffusion of oxygen to any depth in the corroded metal. Figs. 12 and 13 give the results of such traverses. Although the times of exposure for some of the specimens was only 2000 hours, the temperature at this exposure was 1150°F. The 15,000 hour exposure of the 1/2 Cu, 1/2 Mo alloy at 1050°F (Fig. 12) should have been adequate to show any trend. Little broadening of the hardened band at the edges is apparent in the curves. The photomicrograph, Fig. 14a, also shows a narrow hardened band. The exposed specimens appear to be softer, not harder than the original material. To the extent that this trend can be held to exceed the expected scatter of the data the softening effect can be attributed, to some extent at least, to an annealing of residual cold work in the specimen material. With the pure zirconium (Fig. 13), the 1150°F specimens may be slightly harder than the as-received material and there may be a little hardening toward the edges for the 1150°F - 10 ppm specimen. Trends are problematical in both figures and there are no marked effects of changes in water content at 1150°F, or of the 6000 hour exposures at 1050°F for the pure zirconium nor the 15,000 hour exposure of the alloy.

The Effects of Thermal Cycling and Pressure Changes on Weight Gains

It is sometimes contended that the heating and cooling operations necessary for the regular weighing of specimens may result in spalling of the oxide or otherwise introduce errors in weight-gain data. While data derived from intermittent weighing of the specimens might vary from that obtained from a continuously-recording balance technique some thermal cycling would be expected in reactor operation. A large number of rigorous thermal cycles might, however, be expected to accelerate cracking of the protective film and result in a single rate transition, or a series of rate transitions. In view of the possible effects of cycling on rate transitions, and because such cycling might affect the experimental data, an experiment was carried out in which one of the better alloys was cycled 915 times over a 3000 hour period from 1050 to 100°F. The results are shown on Fig. 15. The scatter band represents the results of three separate tests. The specimens in these non-cycled tests were subject to a maximum of seven cooling cycles

FIG. 3-11. The effect of moisture content on weight gain. The curves compare the behavior of four materials in carbon dioxide (1150°F, atmospheric pressure) at three different moisture contents.

FIG. 3-12. Microhardness traverses for the 1/2 Cu, 1/2 Mo (Carborundum) alloy.

FIG. 3-13. Microhardness traverses for commercially pure zirconium (ICI).

- a. Surface hardening effects as shown by the decreased size of the penetration near the surface. Exposure - 1000 hours at 1150°F and atmospheric pressure. 300X

- c. After 12,000 hours at 800°F and 500 psi. A representative area is shown. 300X

- b. After 15,000 hours at 1050°F and 500 psi pressure. An area of unusually strong attack is shown. A layer of hydride needles is evident below the surface. 300X

FIG. 3-14. The 1/2 Cu, 1/2 Mo (Carborundum) alloy after exposure in three experiments.

FIG. 3-15. Effect of thermal cycling on the 1/2 Cu, 1/2 Mo (Carborundum) alloy at 1050°F and atmospheric pressure. Material was subject to 915 cycles from 1050°F to 100°F (25 minutes cooling, 35 minutes heating).

for weighing. The curve for the cycled specimens is at the bottom of, or slightly below, the band. No gross effect is evident, however. A small change in rate may possibly be indicated at about 1500 hours. From the practical standpoint the alloy is not greatly affected by rather rigorous cycling. As a matter of theoretical interest, continuation of the cycling to times beyond 3000 hours might show rate transition phenomenon more clearly.

As the program had the development of a reactor alloy as an objective, and as reactor pressures could be expected to be in the 500 psi range, most tests were carried out at this pressure. However, it was of interest to determine how sensitive corrosion rates were to pressure. Two tests were made at 1050°F under identical conditions except that one test was carried out at atmospheric pressure and the other at 500 psi. Dry (<10 ppm water) gas was used in both cases. Results for two alloys are shown in Fig. 16. For the 1/2 Cu, 1/2 Mo alloy, the curves for the two pressures are so similar that it can be said that pressure in this range has no important effect. This statement does not hold for the tin-containing alloy, however. This alloy, in general, had one of the highest weight gain rates under all test conditions. At low pressure, the weight gain shown is moderate, but at 500 psi the rate is greatly increased. The effects of pressure then vary considerably for the "good" and "bad" alloys. Other data, not shown, also indicate that pressure effects become more apparent for the less corrosion resistant alloys. The lowest curve of Fig. 16, from a test conducted in a dynamic loop, indicates that at 60 ft per second gas velocity and low pressure the behavior of the alloy is quite similar to that under static conditions. The slightly lower weight gain may possibly indicate some loss of oxide to the moving gas stream.

The Effects of Heat Treatment

Experiments comparing the corrosion behavior of the air-cooled, furnace-cooled, and hot-rolled versions of the RMI alloys listed on Table 3 had shown no distinct trends. As these relatively gentle treatments had been carried out from 200°F below the beta transus the lack of any marked beneficial or deleterious effects is not surprising. In contrast, several of the alloys showed distinct effects from treatments from within the beta region. Table 10 lists the results for the five alloys most affected by beta heat treatment. From this table it is evident that the 1/2 Cu, 1/2 Mo alloy showed a negative result in that the heat treatment produced a less resistant material. The other alloys showed decreased weight gains of from 10 to almost 20% when heat treated. While the spread between the heat-treated and non-heat-treated versions of an alloy may diminish with quite prolonged times of exposure, and while the beta treatment might have a deleterious effect on high temperature strength, the table indicates considerable potential value for the treatment.

A study of the structural changes produced by the heat treatments was not within the scope of the program. In brief, metallographic examination showed no unexpected structural changes in the heat treated specimens, nor

were such changes evident in specimens exposed for long times. Figure 14 shows sections of three corroded surfaces. Such surfaces were usually comparatively smooth, with, of course the lower temperatures and shorter exposure times resulting in the smoother surfaces. (Figure 14a compared with 14c) Figure 14b is untypical in that it shows one of the few indications of intergranular penetration observed in the better alloys. The photomicrograph shows the only such area found in a specimen exposed for 15,000 hours at 1050°F. Pitting did occur but was rare in the "good" alloys. Since localized attack was so uncommon, the weight gain data gives a true picture of the corrosion behavior. Hydride needles were usually found in such long exposure material.

Minor imperfections were fairly common in the as-received experimental alloys and would be expected in material produced in small quantities. In preparing specimens efforts were made to avoid any dubious areas in the sheet, but the presence of imperfections can always be expected to have some effect on the experimental data and can explain the presence of at least some areas of localized attack such as, possibly, that shown in Fig. 14b

DISCUSSION

Corrosion Behavior

Two facts of specific interest are apparent concerning the general corrosion behavior of the alloys studied. The first is that rate transition behavior is common, as shown on Figs. 2 and 4. These transitions were more often encountered at exposures of more than 3000 hours. The second is that the comparative quality of any alloy, as compared to other alloys, may vary markedly from temperature to temperature, as shown most clearly in Tables 6 and 7. The most striking behavior is that shown on Table 7 where the best material at 1050°F, the 0.25% silicon alloy, corroded so badly as to have been considered as failed at 1150°F. The change in comparative position of the commercially pure zirconium as shown on Table 6 is also interesting. At 1292°F (700°C) it was the fifth best material while at 1150°F all the alloys were superior to it. However, at 950°F the comparative standing of the material rapidly improved, and at 800°F it was the second best material. At the completion of the 1292°F test it would have been reasonable to drop all alloys showing worse corrosion behavior than pure zirconium on the basis that the alloying additions had been deleterious rather than beneficial. Had this been done, three alloys which are markedly superior to pure zirconium at other temperatures, as shown on the table, would have been dropped. As 1150°F is closer to the practical use temperature for which these alloys are intended, and, in fact, might be a use temperature for some short-time applications, testing at this temperature has direct utility. Whether or not testing at 1150°F can serve in any way as an accelerated test for 1050°F behavior will depend on the necessities of a specific program, but the change in weight gain curves from semi-parabolic at 1050°F to linear at 1150°F, and the marked change in order of merit listings at the two temperatures would not recommend the 1150°F test for anything but 1150°F results. Our evidence has shown that relations between 1050°F behavior and that at temperatures above 1150°F is so indirect that tests at the higher temperatures cannot be used to predict 1050°F behavior. The program has also indicated that it may be dangerous to put too great a reliance in short-term (less than 3000 hour) tests.

To return to the transition rate phenomena, its occurrence might suggest as one possibility that a protective mechanism is latent in the material, and that this mechanism can operate on occasion to slow a high weight gain rate. Griggs et al,⁸ who have reviewed similar behavior in water corrosion, propose that rate transitions occur when the protective layer reaches a critical thickness and cracks. This cracking is then followed by rapid attack but the rate diminishes as the protective film re-forms. It was originally thought that the fairly rigorous thermal cycling in the experiment discussed might accelerate such cracking. However, no clearly evident rate transitions were found in the experiment, as shown in Fig. 15, but as the experiment was for a period of only 3000 hours, the protective film may not have reached a sufficient thickness for cracking to occur. The thickness of the film is not necessarily the only factor controlling cracking. Certainly the crystal structure of the oxide in the protective layer

Table 10 THE EFFECT OF BETA HEAT TREATMENT
ON CERTAIN ALLOYS

<u>Alloy</u>	<u>Heat Treatment</u>	<u>Hours Under Test</u>	<u>Average weight gain mg/dm²</u>	<u>% Difference</u>
1/2 Cu, 1/2 Mo (Carb.)	as-received			
	hot rolled	3500	873	15.7 Less
	beta heat treatment	3500	1036	—
0.12 Pd	as-received			
	hot rolled	2500	1419	—
	beta quenched	2500	1140	19.7 Less
0.01 Ba	as-received			
	alpha furnace cooled	2000	1155	—
	beta heat treatment	2000	961	16.8 Less
0.04 Ce	as-received			
	hot rolled	2500	1112	—
	beta quenched	2500	993	10.7 Less
0.20 Be	as-received			
	hot rolled	2000	1062	—
	beta quenched	2000	860	19.0 Less

FIG. 3-16. The effect of pressure at 1050°F on the behavior of a "good" alloy - 1/2 Cu, 1/2 Mo (Carborundum Metals) - and on a "bad" 0.2% tin alloy.

or the relative amounts of the various possible crystal forms of ZrO_2 present could also be quite important.

Whether or not cracking is important, the thickness of the film is controlled to a large extent by diffusion. Gulbranson and Andrew¹² have found that the controlling mechanism in the oxidation of zirconium is the diffusion of zirconium ions in cation vacancies in the coating. The experimental results of the microhardness traverses reported herein are not out of line with these conclusions. Work on zirconium alloys resistant to attack by oxygen has evidently been quite limited but a group at Argonne⁵ has reported the results of a program which studied the resistance of binary alloys to oxygen at 700°C. Their results can most readily be summarized by reproducing one of their comparison figures as in Fig. 17. Of their best alloys, Group 1 on the figure, the results reported herein are in agreement for the elements Mo, Cu, Ni, Be and Cr, but our data would not support the choice of Co and Fe. The resemblance of oxygen corrosion to carbon dioxide corrosion is probably much stronger than the resemblance of carbon dioxide corrosion to corrosion in water or steam, but the similarities are probably not great enough to permit extrapolations as regards beneficial alloying elements. One explanation for the differences found between oxygen and carbon dioxide corrosion may be the deposition of carbon from the CO_2 as discussed by Gregg, et al.⁹

The Binary Alloy Addition Elements

As shown in the various tables and figures, the following elements have been found to have beneficial effects as constituents of binary zirconium alloys:

Copper
Cerium
Beryllium
Antimony
Vanadium
Nickel
Lead
Barium
Molybdenum
Manganese
Palladium
Chromium

The more effective elements have been placed at the top of the list, but the list does not necessarily reflect the order of merit, as apparently a valid order of merit can only be made for a specified temperature as in Tables 6 and 7. In addition to corrosion resistance, the above list could be used to provide candidate elements to produce high-temperature strength alloys.

Early failures in tests at 1150°F and 1292°F showed that the following elements have marked deleterious effects when used in the quantities listed:

FIG. 3-17. Photoreproduction of a figure from reference 5 comparing the oxidation resistance of several zirconium alloys studied at Argonne.

	<u>Per cent by weight</u>
Titanium	0.75, 0.52, and 0.25
Yttrium	1.75, 0.8, and 0.45
Niobium	17.0, 1.9, 0.88, and 0.44
Tellurium*	1.06, 0.70, and 0.18

O'Driscoll, Tysack and Raine⁴ have reported on several of the elements in the above lists (see Table 5). The results of this program are in general agreement on those elements common to both programs. The use of ultra-low-moisture content CO₂ in the test work of this program may account for minor discrepancies in results.

In view of the number of addition elements reported by O'Driscoll et al,⁴ and in this paper, it is of interest to consider what possible elements remain uninvestigated. Figure 1 identifies in small letters the elements which could not be used for alloying purposes for reactor applications. These elements are:

1. The noble gases
2. The halogens
3. The alkali metals
4. All fissionable or radioactive elements
5. All elements having excessive neutron capture cross sections.

In preparing this figure a cross-section of 20 barns was arbitrarily set as the maximum.

Of the possible alloying elements it will be seen that only a few remain uninvestigated. These are:

Magnesium
Calcium
Strontium
Zinc
Lanthanum
Praseodymium

Barium was favored over calcium and strontium for study in this program

* Sano⁶ when testing in oxygen has reported beneficial effects from tellurium in much smaller quantities. A 160 ppm Te alloy did not reach breakaway in 5000 minutes at 850° as compared with a breakaway time of 2600 minutes for pure zirconium.

as the lower vapor pressure appeared to provide an advantage in preparing the alloy.

The field of possible addition elements has been covered with only a few exceptions and the more beneficial elements selected. The optimum addition percentages have not, however, been clearly established in most cases. Furthermore, there is always the possibility that elements which appear unpromising in certain percentages might produce valuable alloys in other percentages.

Work in this program has been restricted to the binary alloys. A few of them were found superior to the commercial alloys at two temperatures in comparatively short tests. It would seem that, based on present knowledge, a reasonable probability exists of developing ternary, or more complex, alloys which would be definitely superior to the present commercial Cu-Mo-Zr ternaries. Such a development would be simplified if the intended use temperature range could be defined and limited to a narrow range. It should also be noted that the high-temperature creep strength of the present commercial alloys (Fig. 18) provides room for improvement for applications in the 1050°F range.

MECHANICAL PROPERTIES
vs TEMPERATURE

CREEP AT 6000 PSI

Temperature	Time in Hours to Reach Strain of:			
	0.2%	0.3%	0.5%	1.0%
797°F - 425°C	2,450	3,700	-	-
842°F - 450°C	1,140	1,660	3,000	-
887°F - 475°C	400	570	1,200	4,850
932°F - 500°C	80	160	280	900

COMPARATIVE THERMAL NEUTRON CROSS SECTIONS

Grade 41 (ATR) 1/2 Cu, 1/2 Mo	0.22 barns
Grade 32 (Zircaloy-2)	0.22 barns
Grade 21 (Reactor Grade Zirconium)	0.18 barns
Stainless Steel	3.00 barns approx.

FIG. 3-18. Some properties of the Carborundum 1/2 Cu, 1/2 Mo alloy as given by the manufacturer. (Reference 13)

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DEVELOPMENT OF Zr-Nb-Sn ALLOYS FOR REACTOR APPLICATIONS*

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DEVELOPMENT OF Zr-Nb-Sn ALLOYS FOR REACTOR APPLICATIONS

by

H. RICHTER and J. C. TVERBERG

September 5, 1962

Abstract

Binary phase diagrams have been determined for the zirconium-niobium system at two different oxygen contents. Each diagram shows a definite ternary characteristic due to the oxygen content of the zirconium. Ternary phase diagrams were also developed for the systems zirconium-niobium-hydrogen and zirconium-niobium-tin. The latter system showed an extremely sluggish transformation rate. It was found that the corrosion behavior of the zirconium-niobium alloys was very strongly dependent on the heat treatment, the optimum temperature for heat treatment being 580 C. An alloy with exceptionally good properties was developed, its composition $Zr+3Nb+1Sn$. This alloy had corrosion properties equal to those of Zircaloy-2 and strength and creep properties far superior to Zircaloy-2. This alloy is readily welded and can be fabricated into tubes of the sizes required for reactor use. The hydrogen pick-up was found to be less in this alloy than in Zircaloy-2 and the impact strength much better.

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I. Introduction

Ever since the second Geneva Conference on the Peaceful Uses of Atomic Energy in 1958 there has been an increasing interest in the use of niobium containing zirconium alloys as structural and cladding materials in water cooled nuclear reactors. Until that time the only systematic research had been done by Rogers and Atkins¹⁾ in the preparation of their phase diagram, shown in Figure 1. These experimenters used iodide zirconium as the base material and determined the points on the diagram by X-ray, resistance and dilatometric methods. In their diagram β_{Zr} and β_{Nb} are completely miscible in the solid state above 1000 C. The β - α transformation is lowered by niobium additions to 610 C according to the eutectoid reaction

The composition of the eutectoid point was given as 17.5% niobium and the maximum solubility of niobium in zirconium as 6.5% niobium.

²⁾ This work was reviewed by Domagala and McPherson who, on the basis of metallographic findings, assumed the eutectoid reaction temperature as ~800 C and the maximum solubility of niobium in α -zirconium

FIG. 4-1. Zirconium-Niobium Phase Diagram according to B.A. Rogers and D.F. Atkins ¹⁾

Fig.2 Zirconium-Niobium Phase Diagram, Basis Sponge Zirconium with 800 ppm Oxygen

FIG. 4-2.

Fig.3 Zirconium-Niobium Phase Diagram, Basis Jodide Zirconium with 200ppm Oxygen

FIG. 4-3.

as less than 5%. They also reported complete solid miscibility of niobium in β -zirconium only above 1180 C. Bichov, Rozanov and Skorov³⁾ found by dilatometric means on hafnium containing zirconium alloys an eutectoid temperature of 560 C at 12% niobium with 4% niobium soluble in α -zirconium. Ivanov and Grigorovich⁴⁾ gave the value of the maximum solubility of niobium in α -zirconium as 1.5% at 610 C. Emelyanov, Godin and Evsyukhin⁵⁾ reported a maximum solubility of 0.5% niobium in α -zirconium and an eutectoid temperature of 612 C. Knapton⁶⁾ gave a niobium solubility of less than 1% and an eutectoid composition of 20% niobium at 610 C. More recent work by Cox and Lundin⁷⁾ gives the maximum solid solubility at 0.6% niobium and the eutectoid reaction at 20% niobium and 610 C. Another investigation by Bergout⁸⁾ proposed a complete solubility range.

The corrosion behavior of niobium containing alloys was first presented by Ambartsumyan et al⁹⁾ and Ivanov and Grigorovich⁴⁾ Ambartsumyan reported an increase in corrosion rate with an increasing niobium content up to 5% niobium in 350 C water. Ivanov and Grigorovich reported that niobium contents of 0.2% in 350 C water, 0.5% in 400 C steam and 0.75 - 1% in 480 C steam had a "favorable" corrosion resistance. These authors reported a bad influence on the corrosion resistance due to tin additions, but a favorable influence on the strength properties. The Russian authors did not investigate the effect of heat treatment on the corrosion behavior. Dalgaard¹⁰⁾ also investigated the influence of tin, but

limited his work to 2.5% niobium. More recently¹¹⁾ Dalgaard has reported the corrosion resistance of the 2.5% niobium alloy is increased to a small extent by the addition of copper. Douglass and¹²⁾ Dearing first showed the effect of heat treatment on a Zr+2Nb+2Sn alloy. Douglass later showed¹³⁾ that a beta phase heat treatment (above 800 C) had a very bad influence on the corrosion behavior.¹⁴⁾ Klepfer showed that niobium containing alloys annealed at 590 C have a far better corrosion resistance than those annealed in the beta phase region. Klepfer also found that the zirconium-niobium alloys picked up less hydrogen from steam corrosion than did¹⁵⁾ Zircaloy-2. Burton indicated that the corrosion resistance of the 2.5% niobium alloys decreases very rapidly with steam temperatures up to 500 C. Rosenfeld et al¹⁶⁾ has shown that the presence of F^- , Cl^- , SO_4^{2-} and CO_3^{2-} ions in reactor water causes increased corrosion in 360 C water with zirconium-niobium alloys.

The bulk of the mechanical properties and creep properties for zirconium-niobium alloys were presented at the second Geneva Conference.⁹⁾ Ambartsumyan et al have determined creep behavior for the alloys Zr+1Nb and Zr+2.5 Nb, made from iodide zirconium, at temperatures between 300 and 450 C. After 500 hours at 350 C their alloys showed a strain of 0.2% at a stress of 15 kg/mm^2 (21, 300 psi) and 0.2% strain at 450 C at a stress of 3 kg/mm^2 (4,300 psi).⁴⁾ Ivanov and Grigorovich observed an improvement in the creep behavior of the alloy Zr+4Nb+1Sn and the alloy with 1 - 2 Sn+2Nb¹⁷⁾ at the same stresses. Douglass later showed that the creep

properties were improved by quenching from the beta zirconium phase. The same effect was observed by annealing at 800 C followed by a slow cooling. The American experimenters Adamson et al¹⁸⁾ have presented much aging data on a Zr+15Nb alloy. Ambartsumyan et al⁹⁾ showed that the tensile strength increases with the niobium content from 25 kg/mm² (35,500 psi) for pure zirconium at 20 C up to 65 kg/mm² (92,400 psi) at 5% niobium and 10 kg/mm² (14,200 psi) at 500 C for pure zirconium to 35 kg/mm² (49,800 psi) at 5% niobium. The 5% niobium alloy showed a slight decrease in elongation with increasing temperature from 19% at 20 C to 18% at 500 C, and a slight increase in reduction-in-area values from 49% at 20 C to 50% at 500 C. All alloys were annealed at 700 C to give the maximum strength. Ivanov and Grigorovich⁴⁾ have shown the strength properties of zirconium-niobium alloys increase with increasing niobium content up to 30% niobium. The maximum strength is attained at 20 C at about 5% niobium. At 500 C two peaks are found, one at about 4.5% niobium and a slightly higher peak at 15% niobium. The maximum 0.2% offset yield strength was given at 72 kg/mm² (102,400 psi) at 5% niobium and 20 C, the proportional limit at 70 kg/mm² (99,500psi) and the ultimate tensile strength at 75 kg/mm² (106,500 psi). The same values at 500 C are 51 kg/mm² (72,500 psi), 50 kg/mm² (71,100 psi) and 60 kg/mm² (85,300 psi) respectively. These alloys were heat treated 24 hours at 500 C. These authors also found that the 20 C strength reached a low value in a 1% tin alloy with 2% niobium, but regained the strength at 5% tin. At 500 C the 3% tin alloy had the highest strengthening values, almost doubling the Zr+2Nb alloy at 500C.

The application of these alloys to reactor systems has been made only by the Russians at the present time. At the Salzburg Corrosion Conference Kiselev¹⁹⁾ indicated that the Zr+1Nb alloy was being used as cladding material in submarine reactors, while both Zr+1Nb and Ozinite 0.5 (0.2% Sn + 0.1% Fe + 0.1% Ni + 0.1% Nb) were used as cladding material in the Voronesh Power Station and that Zr+2.5%Nb is used in pressure tubes and as a construction material where the corrosion attack is lower. All of these Russian alloys are made from iodide zirconium.

Information on the irradiated material is scarce*. The Russians mentioned¹⁹⁾ that a neutron flux of $5 \times 10^{13} - 3 \times 10^{14}$ n/cm²/sec has had no influence on the mechanical properties of the Zr+2.5%Nb alloy after 1½ years. The corrosion properties of this alloy in a neutron flux are being determined.

III. Phase Equilibrium Investigations

Binary Zr-Nb System²⁰⁾

An examination of the previous work indicated several important observations:

Nb Solubility in Zr: The highest values of 6.5 and 4% niobium were the results of dynamic measuring methods while the lower values of 1.5 and 0.5% niobium were obtained by metallographic means.

*Since the preparation of the original manuscript C. R. Cupp has reported on the effect of neutron irradiation on the mechanical properties of a Zr+2.5%Nb alloy in the August issue of the Journal of Nuclear Materials.

Eutectoid Temperature: The temperature of 800 C given by Domagala and McPherson appears too high and may be due to a misinterpretation in the quenched 15% niobium alloy. The very low temperature of 560 C given by Bichkov was obtained by dilatometric means as is probably due to the very sluggish adjustment of the equilibrium. Adamson pointed out the existence of this very slow reaction. The value of 610 C found by Rogers and Atkins was assumed in most of the other work.

Eutectoid Composition: There is much disagreement in the literature on the composition of the eutectoid point varying between 12 and 20% niobium. These differences are due to the sluggish adjustment of the equilibrium.

On the basis of these observations an investigation was undertaken using zirconium with two different oxygen contents. The first group of alloys were made from sponge zirconium with an average oxygen content of 800 ppm, the second group were made from iodide zirconium and had an average oxygen content of 200 ppm. As all commercial alloys are made from sponge zirconium for economic reasons, it is very important to know the effect of oxygen on the phase equilibrium in order to determine the proper heat treatment. Figure 2 shows the results of this investigation. In a similar manner the phase equilibria for zirconium-niobium alloys made from iodide zirconium was determined and is presented in Figure 3. In both of these alloy systems oxygen is seen to exert a distinct ternary characteristic to the binary system creating a three

component field, namely $\alpha_{\text{Zr}} + \beta_{\text{Zr}} + \beta_{\text{Nb}}$. Thus, each of these binary diagrams correspond to a vertical cut through the Zr-Nb-O system at about 0.08% and 0.02% oxygen. The oxygen content causes an extension of the α - transformation interval which is in agreement with the observations of Lundin²¹⁾ on unalloyed zirconium. Betterton and Easton²²⁾ also observed this phenomenon in their investigation of the silver-zirconium system.

Figures 2 and 3 represent the results of metallographic and resistance measurements. The lower limit of the homogenous β_{Zr} field is displaced to considerably higher temperatures by the oxygen content. This is identified by point "B" on both diagrams and is hereafter called the eutectoid point. It is seen that the eutectoid temperature limit (line EF) is also lowered to 590 C. In the iodide alloys this line gradually increased to 610 C which is the value given by Rogers and Atkins. This lower limit of transformation was detected by electrical resistance measurements. In later work corrosion results on alloys annealed between 580 and 625 C clearly showed a sharp increase in the corrosion rate at 595 C indicating that a structural change had occurred. Thus, the value of 590 C appears to be the actual transformation limit in alloys made from sponge zirconium as shown by several entirely different methods. The maximum solubility of niobium in alpha zirconium as found by metallographic examination lies between 1.5 and 2% niobium at 585 C for the alloys made from sponge zirconium and 2.0 and 2.5% niobium at 585 C for the alloys made from iodide zirconium. X-ray

investigation yielded a lower value of 1 - 1.5% niobium. In both systems the eutectoid point "B" lies at 19% niobium with a temperature of 815 C for sponge zirconium and 705 C for the iodide zirconium alloys. This results in a transformation spread of almost 200 C for sponge zirconium alloys and 100 C for iodide zirconium alloys.

23)

Ternary Zr-Nb-H-System

During the corrosion of zirconium alloys in water and steam, hydrogen is produced as an undesirable corrosion by-product. The extent of this hydrogen pick-up during corrosion depends mainly on the temperature of the corroding media and can be influenced by alloy additions and the heat treatment.

24)

The work of Libowitz²⁴⁾ was used to update the hydrogen rich portion of the zirconium-hydrogen diagram appearing in Hansen's "Constitution of Binary Alloys"²⁵⁾. The revised diagram is presented in Figure 4.

A comparison of Figure 4 with Figures 2 and 3 shows that both niobium and hydrogen lower the α - β transformation temperature and expands the temperature interval in which the transformation occurs. While it is possible to retain the stable β_{Zr} phase in zirconium alloys with up to 10% niobium by quenching, it is not the case with hydrogen rich zirconium alloys, instead the β -phase decomposes into alpha zirconium and the tetragonal delta hydride. The maximum solubility of hydrogen in alpha zirconium is about 7 a/o.

Figure 5 presents the derived isothermal sections at 540, 590, 700 and 900 C. The alloy composition is expressed in atomic percent to

by M. Hansen u. K. Anderko¹⁵⁾ und G. C. Libowitz²⁴⁾

FIG. 4-4 PHASE DIAGRAM ZIRCONIUM HYDROGEN

915-9

a) Isothermal section at 540°C

b) Isothermal section at 590°C

c) Isothermal section at 700°C

- 1 Phase
- 2 Phases
- ▲ 3 Phases
- H Hydride

d) Isothermal section at 900°C

M

FIG. 4-5
Zirconium Rich Corner of the Ternary System Zr-Nb-H. Isothermal Section taken at 540, 590, 700 and 900°C.

Met Lab
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allow better clarity for the hydrogen values. All alloys used in this investigation were melted from sponge zirconium, thus a constant value of 800 ppm oxygen is present, existing in the dissolved form. At 900 C it is seen that a portion of the α_{Zr} phase is still present in the form of $\alpha + \beta_{\text{Zr}}$ which is probably due to the dissolved oxygen. At 700 C the $\alpha + \beta_{\text{Zr}}$ field is expanded at the expense of the β_{Zr} field. The hypothetical position of the $\alpha_{\text{Zr}} + \beta_{\text{Zr}} + \beta_{\text{Nb}}$ field has been sketched in to indicate the approximate location. A small portion of α_{Zr} is also present. Lowering the temperature to 590 C, which is just slightly over the eutectoid temperature in the zirconium-niobium system, causes hydrogen additions to stabilize the β_{Zr} phase which appears in the martensitic form. During quenching of the alpha zirconium phase, modified needle hydride precipitates appear due to a decrease in the hydrogen solubility. At 540 C hydrides begin to appear and the β_{Zr} phase can be stabilized by as little as 3.5 a/o hydrogen (300 ppm). This is extremely bad for the corrosion resistance as will be shown later in this paper. A more complete description of this system is available from the ²³⁾ EURATOM Technical Report Service .

. 26)

Ternary Zr-Nb-Sn Systems

The zirconium rich portion of the Zr-Sn-Nb system was investigated in the temperature interval between 575 and 750 C. Both metallographic and X-ray techniques were used to evaluate the alloys melted from sponge zirconium. The existing work on this system, which had ²⁷⁾ been done by Bibb , is shown in Figure 6. This work used iodide

FIG. 4-6. Isothermal Sections in the System ZrNbSn for Iodide Zirconium, According to A. E. Bibb²³⁾

FIG. 4-7. Zirconium Rich Corner of the Ternary System ZrNbSn. The Isothermal Sections are taken at 590, 610, 650 and 750 C (Alloys based on Sponge Zirconium)

zirconium and contained no information on the temperature interval of 500 - 725 C which is very important in the heat treatment of these alloys.

Figure 7 presents the isothermal sections at 590, 610, 650 and 750 C. Here, the solubility of tin in alpha zirconium increases with increasing temperature in this temperature range while the niobium solubility decreases. The equilibrium reaction is extremely sluggish in the range of 590 to 650 C and is not complete even after 100 hours of annealing. This is a very important point to consider in selecting the duration of heat treatment in this temperature range. Again, a more detailed description will be found in either the original or translated report available from the EURATOM Technical Report Service (Reference 26).

III. Effect of Alloy Additions on the Corrosion of Zirconium Alloys

Zirconium-Niobium Alloys

To include all of the corrosion testing data which has been done on the zirconium-niobium alloys would fill a volume in itself. Therefore, for those who are interested in the details of our corrosion work, we refer you to our original work which is available through EURATOM. These reports are listed in the references as Numbers 28, 29, 30 and 31.

In general the corrosion behavior showed a distinct dependence on the structural condition. Figure 8 presents the weight gain of three alloys $Zr + 1Nb$, $Zr + 3Nb$ and $Zr + 3Nb + 1Sn$ after 1720 hours

FIG. 4-8 Corrosion in 400 C Steam as a Function of the Heat Treatment. Corrosion Time 1720 Hours.

corrosion in 400 C steam. The specimens annealed under the alpha-beta transformation region had the best corrosion behavior. This structure is shown in Figure 9a and can be compared to the structure of material annealed above the transformation temperature shown in Figure 9b. The more corrosion resistant structure contains β_{Nb} in an α_{Zr} matrix and the corrosion prone structure contains β_{Zr} in the α_{Zr} matrix. As seen from Figure 8, the transformation range is associated with an increase in the corrosion rate. From these data it is apparent that the most satisfactory corrosion resistant material occurs when the annealing treatment takes place below 590 C. For this reason a temperature of 575 C and a duration of 10 days was initially specified as the heat treatment.

Figures 10, 11 and 12 show the corrosion curves for five niobium containing alloys as compared to Zircaloy-2. Conditions for the corrosion testing were 350 C water and 400 and 480 C steam at two heat treatments 575 for 10 days with an air cool and 650 C for 1 hour with an air cool. In 350 C water the curves appear as straight lines and the specimens annealed at 575 C show no marked difference and lie within the scatter-band for Zircaloy-2. However, the specimens annealed at 650 C show an increase in the corrosion rate with the niobium content. At 400 C the specimens annealed at 575 C show a definite break in the weight gain-time curve at about 1000 hours, but without a visible change in the surface condition (i.e. no breakaway) associated with the steeper portion of the curve. Also there was essentially no difference in the individual alloys

and no systematic dependence on the niobium content. Furthermore, these curves lie within the scatter-band for Zircaloy-2. Once again the higher annealing temperature produced a higher weight gain. The specimens corroded at 480 C have a much higher corrosion rate and because of higher temperature the effect of the heat treatment is less. The comparative values for Zircaloy-2 lie between the values for the various zirconium-niobium alloys.

The reason for the stable surface condition even after a kink in the curve or change in corrosion rate appeared is probably due to two causes. The first is a higher solubility of hydrogen in the lattice and the second is a faster instantaneous initial corrosion rate. This later point is illustrated by considering some electrochemical measurements made on several zirconium alloys as shown in Figure 13. These curves show that in both cases the niobium containing alloys are passivated at a faster rate than Zircaloy-2, and that the material annealed at 580 C is passivated at a faster rate than the material annealed at 800 C. This would indicate that any cracks in the oxide layer would heal faster than in Zircaloy-2, which would also decrease the amount of hydrogen pick-up.

ZrNbSn Alloys

Figure 14 illustrates the effect of 0.5 to 1.0% tin for various zirconium-niobium alloys after 3000 hours in 350 C water, 2000 hours in 400 C steam and 1000 hours in 480 C steam. Tin additions had a beneficial effect in the material heat treated at 575 C and corroded in 350 C pressurized water. At 400 C the tin had practically no

a) $\alpha + \beta_{Nb}$ Structure in the alloy
ZrNb₃Sn₁ obtained by annealing
16 hours at 575 C with an air cool.

b) $\alpha + \alpha_{Zr}$ Structure in the alloy
ZrNb₃Sn₁ obtained by annealing
1 hour at 700 C with an air cool.

FIG. 4-9 Photomicrographs of the two Structures obtained by Heat Treatment. a) is Corrosion Resistant b) is Corrosion Prone.

Weight Gain-Time Curves for
Various Zirconium-Niobium Alloys in 350°C
Water at 170 Atm (2200psi)

FIG. 4-10

Weight Gain-Time Curves for Various Zirconium-Niobium-Alloys in 400°C Steam at 200 Atm. (3000 psi)

FIG. 4-11

Weight Gain-Time Curves for Various Zirconium-Niobium Alloys in 480°C Steam at 200 Atm. (3000 psi)

FIG. 4-12

FIG. 4-13

Corrosion of Various Zirconium-Niobium-Tin-Alloys in Pressurized Water and Steam.

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influence and has an unfavorable influence in 480 C steam. When heat treated at 650 C the tin additions have a poor corrosion resistance in all media, especially at 480 C.

It was on the basis of this work that the final alloy composition $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ was chosen. This particular alloy will be covered in detail in a later section of this paper.

Zr-Nb-Sn-Pd Alloys

A palladium content of 0.2% had a very bad effect on the corrosion resistance of all investigated alloys, leading to considerably higher weight gains. This is a distinct contrast to unalloyed zirconium⁴¹⁾ where a palladium content showed a distinct improvement.

Zr-Nb-Sn-Cr and Zr-Nb-Sn-Mo Alloys

An addition of 0.3% Cr to the alloy $\text{Zr} + 2\text{Nb} + 1\text{Sn}$ had no noticeable effect on the corrosion behavior. An equal molybdenum addition led to a higher weight gain.

IV. Corrosion Behavior of the $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ Alloy³²⁾

Because of the favorable properties shown by this alloy during the survey corrosion testing, this alloy was selected for further investigation. The corrosion behavior of this alloy is shown in Figure 15 as compared to $\text{Zr} + 2\text{Nb}$ and Zircaloy-2. Annealing this alloy at 580 C results in essentially the same corrosion properties as Zircaloy-2 and does not show a spalling or a breakaway corrosion product in the time of testing (up to 5000 hours³¹⁾). A detailed investigation on the effect of heat treatment showed that the

FIG. 4-15. Comparative Corrosion Curves for
Zr + 3% Nb + 1% Sn, Zr + 2% Nb
and Zircaloy-2

FIG. 4-16. Hydrogen Pickup Rate from a Hydrogen Atmosphere
at 575 C. Specimens 10 mm dian (0.34 in.) and
40 mm long (1.575 in.).

optimum heat treating temperature was 580 ± 10 C. The length of time at this temperature is necessarily long as governed by the sluggish transformation rate. An annealing time of four hours is sufficient to provide sufficient precipitation of the β_{Nb} phase to provide good corrosion properties.

Material cold worked up to 60% was found to have only a slightly higher corrosion rate than the completely annealed material at times up to 3000 hours. This is in agreement with the results^{34,35)} obtained for Zircaloy-2 and pure zirconium

The effect on the corrosion rate due to small variations in the niobium and tin contents from the nominal values of 3% niobium and 1% tin were also investigated³³⁾. A somewhat higher corrosion rate was found at 3.5% niobium and 1.5% tin in each case. The hydrogen pick-up was not influenced by a variation in the tin content between 0.5 and 1.5%, but because of the poorer corrosion resistance at 1.5% tin it is advisable to limit the tin content to $1 \pm 0.15\%$. Small variations in the niobium content showed no noticeable effects on either the corrosion or hydrogen pick-up rates except at 3.5% niobium. Thus, the niobium limits have been set at $3 \pm 0.25\%$.

It is possible to age harden this alloy, that is, to place the alloy in a different structural condition by quenching from a higher temperature, then aging at lower temperatures to restore the corrosion resistance. It was found that quenching from the beta zirconium solid solution ranges of 700, 800 and 1000 C an aging treatment at

550 C leads in all cases to a softening. Aging the specimens annealed at 700 and 800 C at 350 and 450 C led to an age hardened condition while the specimens quenched from 1000 C maintained the original hardness when annealed at both 350 and 450 C. Comparing the corrosion behavior of these differently aged specimens showed in all cases that the corrosion resistance was poorer than the specimens annealed at 575 C. Relatively speaking, the best corrosion resistance was associated with the lowest hardness which confirms the findings that the heat treatment which results in an increase in the strength properties in each case is made at the expense of the corrosion behavior^{13,28)}

V. Hydrogen Pick-Up

Hydrogen pick-up in zirconium alloys is of great importance as the presence of hydrogen greatly affects the mechanical properties, particularly the impact strength, causing a noticeable decrease in the strength. This hydrogen is released in the atomic state during the corrosion of zirconium thus:

This atomic hydrogen can either combine into molecular hydrogen or else react in the atomic state forming the hydride.

The rate at which several zirconium alloys pick-up hydrogen from a hydrogen atmosphere is shown in Figure 16. Here it is seen that Zircaloy-2 has the fastest pick-up rate, Zr + 2Nb the slowest and with Zr + 3Nb + 1Sn lying close to Zr + 2Nb. The actual hydrogen pick-up values for several zirconium-niobium alloys are given in

Table 1. These values are reported in both percent of the total hydrogen picked up and in mg/dm^2 . This manner of presentation provides an equitable basis of comparison with the weight gain. The hydrogen pick-up of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ melted by several methods, at several heat treatments and the corrosion properties are compared with Zircaloy-2 and several variations of the $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ alloy in Table 2. These data show that during corrosion in 350 C water and 400 C steam the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ picks up less hydrogen than Zircaloy-2 and at 480 C the hydrogen pick-up is about the same as Zircaloy-2. The hydrogen pick-up increases with an increasing annealing temperature, but not as rapidly as the oxidation rate.

In a separate metallurgical investigation, the effect of hydrogen additions on the alloys $\text{Zr} + 3\text{Nb}$ and $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ was studied. It was found that the tin remained in the dissolved form so that no new phase appeared. However, a harsh quench from both 700 and 900 C always produced hydride precipitates, but in slowly cooled specimens these precipitates did not appear. Figures 17 and 18 show the photomicrographs of these structures after a 900 C harsh quench and slow cooling also from 900 C.

At 700 C, 430 ppm hydrogen was found to be completely in the beta zirconium phase. Harsh quenching preserves this phase but the hydride forms because the hydride solubility decreases with decreasing temperature. Slower cooling produces the beta niobium phase which can dissolve a larger amount of hydrogen, thus the

TABLE I.

Hydrogen Pickup in Zirconium-Niobium Alloys during Corrosion

Alloy	Annealing Treatment	Test Temp.	Time at Temp.	Wt. Gain mg/dm ²	H ₂ Pickup ppm	% of Total H ₂ Picked Up
Zr + 0.5Nb	590 C/Air	400 C	84 Days	73	127	31
Zr + 1 Nb	1000 C/Water	"	"	101	92	13
Zr + 1 Nb	590 C/Air	"	"	84	194	33
Zr + 2 Nb	700 C/Air	"	"	178	232	17
Zr + 3 Nb	625 C/Water	"	"	164	255	14
Zr + 3 Nb	590 C/Air	"	"	76	72	9
Zr + 5 Nb	590 C/Air	"	"	264	211	13
Zr + 2Nb + 1Sn	590 C/Air	"	"	167	240	17
Zr + 0.5Nb	590 C/Air	480 C	42	128	67	24
Zr + 2 Nb	590 C/Air	"	42	209	326	23
Zr + 3 Nb	575 C/Air	"	83	532	1020	48
Zr + 3 Nb	650 C/Air	"	83	485	790	31
Zr + 5 Nb	590 C/Air	"	42	174	312	22
Zr + 2Nb + 1Sn	590 C/Air	"	42	250	452	22
Zr + 3Nb + 1Sn	575 C/Air	"	83	779	990	19
Zr + 3Nb + 1Sn	650 C/Air	"	83	723	450	14
Zircaloy-2	600 C/Air	"	42	237	380	38
Zircaloy-2	650 C/Air	"	83	267	420	39
Zircaloy-2	650 C/Air	"	83	+))	2200	--

+)Spalling Oxide

Table II

Hydrogen Pickup in Zirconium Alloys during Corrosion in Water and Steam

Alloy	Method of Melting	Heat Treatment	Corrosion			Wt. Gain mg/dm ²	Hydrogen Pickup mg/dm ²	% Hydrogen picked up of the Theoretical Value
			Media	Temp.	Time			
Zr + 3Nb+1Sn	Vacuum	4 h 575°C	steam	400	2729	111.8	2.83	20
"	"	16 h 575 "	"	"	"	116	3.94	27
"	"	4 h 595 "	"	"	"	126	4.17	26
"	"	4 h 625 "	"	"	"	231	4.41	15
"	"	16 h 625 "	"	"	"	313.5	4.90	13
Zr + 3Nb+1Sn	Vacuum	16 h 575°C	steam	400	3400	124	3.23	21
"	"	+15% Cold Work	"	"	"	128	2.26	16
"	"	+50% Cold Work	"	"	"	137	3.37	22
Zircaloy-2	"	16 h 575°C	"	"	"	110	2.87	20
"	"	+15% Cold Work	"	"	"	126	3.00	19
"	"	+15% Cold Work	"	"	"	130	3.53	22
Zr+2.5Nb+1Sn	Argon	16 h 575°C	water	350	3026	36.7	0.37	8
Zr + 3Nb+0.5Sn	"	"	"	"	"	41.9	0.53	9
Zr + 3Nb+1Sn	"	"	"	"	"	40.3	0.54	9
Zr + 3Nb+1.5Sn	"	"	"	"	"	52.5	0.60	9
Zr+3.5Nb+1Sn	"	"	"	"	"	45.7	0.71	12
Zircaloy-2	"	"	"	"	"	36.1	1.59	35
Zircaloy-2	"	"	"	"	"	34.9	1.01	23
Zr+2.5Nb+1Sn	"	"	steam	400	3023	214	4.22	16
Zr + 3Nb+0.5Sn	"	"	"	"	"	142	3.23	10
Zr + 3Nb+1Sn	"	"	"	"	"	230	4.03	14
Zr + 3Nb+1.5Sn	"	"	"	"	"	303	4.08	11
Zr+3.5Nb+1Sn	"	"	"	"	"	167	2.52	12
Zircaloy-2	"	"	"	"	"	158	6.40	32
Zircaloy-2	"	"	"	"	"	141	5.40	28
Zr+2.5Nb+1Sn	"	"	steam	420	1003	346	10.5	24
Zr + 3Nb+0.5Sn	"	"	"	"	"	231	12.7	23
Zr + 3Nb+1Sn	"	"	"	"	"	466	6.0	10
Zr + 3Nb+1.5Sn	"	"	"	"	"	500	14.15	23
Zr+3.5Nb+1Sn	"	"	"	"	"	306	3.8	33
Zircaloy-2	"	"	"	"	"	240	5.0	30
Zircaloy-2	"	"	"	"	"	200	8.3	34

FIG. 4-17.

Water Quenched from 900°C

FIG. 4-18.

Furnace Cooled from 900°C

Alloy
Zr + 3 Nb + 1 Sn
with
532 ppm Hydrogen

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slower cooled specimens show no hydride precipitates. This is very important in reactor fuel cladding or in structural components as the corrosion produced hydrogen will remain in solution and not precipitate. If precipitation did occur, these precipitates could form internal stresses in the oxide layer which could lead to cracks in the film and eventually to spalling of the oxide film. The higher solubility of hydrogen in beta niobium could also aid in the better corrosion behavior shown by the material annealed at 580 C in which beta niobium is present. However, the oxide film of the material annealed in the beta zirconium range probably cracks due to stresses caused by decomposition of the metastable beta zirconium at the corrosion temperature.

VI. Mechanical Properties

The creep properties of the zirconium-niobium alloys have been investigated by numerous research workers as was covered in the Introduction. Although the results obtained by these workers are very useful, it is not possible to obtain the low creep limits of $\sigma_{0.1}/1000$ hours because of the very high loads and very short times which led to strains of 1% and more.

Figure 19 presents the results of the tensile tests for the alloys Zr + 2Nb, Zr + 3Nb + 1Sn and Zircaloy-2 at several heat treatments and as a function of the test temperature. The tensile strength and the $\sigma_{0.1}$ and $\sigma_{0.02}$ yield strength increase as the final annealing temperature increases. In all cases the strength of the niobium containing alloys is higher than that of Zircaloy-2. This was true

FIG. 4-19

even when the niobium containing alloys were given the heat treatment to make the corrosion properties a maximum at the expense of the mechanical strength.

Niobium was found to improve the low temperature creep properties and tin was found to improve the high temperature creep behavior. This latter point explains the good high temperature strength properties of Zircaloy-2 as compared to unalloyed zirconium. An alloy containing both tin and niobium should have good creep properties at both high and low temperatures. This is the case as shown in Figures 20 and 21 in which the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ is much stronger than either $\text{Zr} + 2\text{Nb}$ or Zircaloy-2, in fact it is almost twice as strong as Zircaloy-2 at 250 C. The excellent creep behavior¹⁷⁾ which Douglass reported by quenching from a higher temperature were determined for only short creep times. It was found in this investigation during the age hardening tests that prolonged testing at 450 C leads to a slow decomposition of the beta zirconium phase, thus to a softer structure. If this material was heat treated for high strength and then used at temperatures of 450 C or higher, a much higher creep rate could result due to repeated cycling into the transient creep stage associated with phase transformation. At the lower temperatures of 300 C or less this process would occur so slowly that there would probably be no change in the creep properties in the useful lifetime of the alloy. More complete creep data are^{28,29,31,36 and 37)} to be found in references , all available from the EURATOM Publication Service.

FIG. 4-20. Permanent Strain as a Function of the Stress after 2000 hr Creep Time. (To convert from kg/mm^2 to psi multiply by 1422.)

FIG. 4-21. Stresses Required to Produce a Creep of 0.1 or 0.4% in 1000 hours in Several Zirconium Alloys at Different Temperatures. (To convert from kg/mm^2 to psi multiply by 1422.)

Hydrogen exerts a considerable influence on the mechanical properties of the alloys $\text{Zr} + 2\text{Nb}$, $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ and Zircaloy-2. The results of the hardness measurements on the specimens quenched from various temperatures are presented in Figure 22 as a function of the hydrogen content. All of the investigated alloys show an increase in hardness with an increasing hydrogen content up to a maximum, at which point the hardness decreases or else remains constant. The maximum hardness value is associated with the formation of the largest quantity of omega phase from the beta zirconium phase during quenching. The effect of hydrogen on the tensile properties is given in Table III. Hydrogen additions had practically no influence on the strength and yield limits of Zircaloy-2, however the ductility values were reduced by more than half. At equal elongations the decrease of the niobium containing alloys are less than for Zircaloy-2. The yield limits 0.02 and 0.1 for the alloys $\text{Zr} + 2\text{Nb}$ and $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ are lowered by hydrogen additions, but not so much as Zircaloy-2. The yield limits of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ showed the least decrease. The tensile strengths of both niobium containing alloys were increased considerably by the addition of hydrogen. The difference in behavior is more clearly shown in the true stress-strain curves of Figures 23 and 24. The stress-strain curves for the niobium containing alloys are steeper than those of Zircaloy-2 which indicates that work hardening through deformation is greater when hydrogen is present. Hydrogen additions in Zircaloy-2 cause only a slight influence on the work hardening ability. Work hardening is of great importance in analyzing the results of the creep tests.

FIG. 4-22

FIG. 4-23 INFLUENCE OF HYDROGEN ON THE WORK-STRENGTHENING OF ZIRCONIUM ALLOYS AT 350 °C.

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915-11

FIG. 4-24 INFLUENCE OF HYDROGEN ON THE WORK-STRENGTHENING OF ZIRCONIUM ALLOYS AT 20 °C.

Table III

Mechanical Properties of Hydrogen Loaded Specimens at 20 and 350°C
Heat Treatment 16 h 575°C
(Multiply by 1422 to Convert kg/mm² to psi)

Alloy	Hydrogen Content ppm	Test Temp. °C	Yield Strength (kg/mm ²)				Tensile Strength σ_B (kg/mm ²)	Elongation ϵ_{10} (%)	Reduction in Area (%)
			$\sigma_{0.02}$	$\sigma_{0.05}$	$\sigma_{0.1}$	$\sigma_{0.2}$			
Zircaloy-2	-	20	16.4	19.8	23.2	26.2	41.0	30	57
"	506	20	19.0	22.8	26.0	29.0	46.8	15	39
"	1030	20	17.6	21.6	25.8	-	42.0	11	14
Zr + 2Nb	-	20	33.0	35.8	38.8	41.6	51.1	24	69
"	509	20	25.6	30.0	35.0	40.0	55.2	13	52
"	1200	20	25.6	32.7	38.8	44.6	72.6	13	46
Zr + 3Nb+1Sn	-	20	30.0	41.0	44.0	47.2	57.3	26	74
"	513	20	25.8	35.8	40.8	46.0	66.8	11	48
"	1020	20	29.0	38.4	47.0	51.9	71.9	8	45
Zircaloy-2	-	350	5.7	8.0	9.0	10.0	19.7	43	79
"	520	350	9.3	11.6	13.2	14.8	21.4	30	78
"	1070	350	8.2	10.7	12.9	15.0	23.0	28	76
Zr + 2Nb	-	350	22.0	25.1	26.9	28.2	34.1	22	80
"	491	350	17.0	21.4	24.5	27.2	36.2	18	77
"	1150	350	16.0	21.2	25.3	30.4	42.4	13	74
Zr + 3Nb + 1Sn	-	350	28.4	30.0	31.5	33.1	39.0	23	82
"	518	350	21.5	26.5	31.0	34.3	44.0	14	75
"	1020	350	21.2	27.7	33.6	40.3	58.8	14	65

The effect of hydrogen on the creep properties is shown in Figure 25. Creep curves of hydrogen free and hydrogen containing Zircaloy-2 show only a slight difference at a stress of 6 kg/mm^2 (8,600 psi), however, the creep at 350 C is worsened by hydrogen as well as at the higher stresses by minor additions of hydrogen. The creep elongation of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ was greatly reduced at the high stress of 14 kg/mm^2 (19,900 psi) which led to 0.7% elongation after 5000 hours in the hydrogen free specimens. This effect is probably due to the work hardening effect which is discussed more in detail elsewhere ²³⁾

Hydrogen contents of 50-500 ppm cause a sharp decrease in the impact strength of Zircaloy-2 at higher temperatures ³⁵⁾. The niobium containing alloys show a distinct influence of hydrogen on the temperature dependence of the impact properties. The specimens were 6 mm diameter Izod rods. Figure 26 presents the comparative impact curves. Zircaloy-2 shows a decrease in the impact strength at 200-500 ppm hydrogen with the shift occurring at 200 ppm hydrogen at 260 - 320 C or at 500 ppm to over 400 C. The impact strength is reduced in the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ at 20 C, however at 200 ppm hydrogen this alloy has the same impact strength as hydrogen free Zircaloy-2 specimens. At 500 ppm hydrogen and 200 C the impact strength of the $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ alloy is always higher than the impact strength of hydrogen free Zircaloy-2. The impact curves for hydrogen containing and hydrogen free specimens cross at 300 C. This alloy will never attain the same favorable impact behavior as the alloy $\text{Zr} + 2\text{Nb}$, but even so the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ has much better impact properties than

FIG. 4-25.

FIG. 4-26.

Zircaloy-2. The cause of this different behavior in the niobium containing alloys is that the hydrogen is dissolved at the higher temperatures and consequently no embrittlement results, while at the lower temperatures the hydrides precipitate, thus lowering the toughness. On the basis of Figure 26 it can be assumed that the hydrogen in Zircaloy-2, which has tin as the main alloying ingredient, goes into solution at a higher temperature than the alloy $\text{Zr} + 2\text{Nb}$. The hydrogen solubility of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ takes place at temperatures which lie midway between the transition temperatures of the other two alloys. Thus, the temperature dependence for the impact values of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ lies between those for Zircaloy-2 and $\text{Zr} + 2\text{Nb}$.

VII. Engineering Properties

Fabrication

The alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ can be easily fabricated into tubes by a combination of extrusion, cold rolling (Rockrite Process) and drawing. The arc melted ingots were center bored and clad in a gas tight copper can. Extrusion took place at 830 C which was a compromise temperature. If extruded at a lower temperature the press power requirements would become excessive, and if at a higher temperature the copper-zirconium eutectic would form at 885 C. At this temperature the alloy lies in the $\alpha_{\text{Zr}} + \beta_{\text{Zr}}$ transformation range. In contrast to Zircaloy-2, hot working in this range does not lead to the precipitation of large particles of intermetallic compounds, but rather to a fine transformation structure.

In order to simplify the further processing it was found to be best to extrude a tube with a fairly thick wall. In our work this meant extruding to a 82% reduction or to a tube 45 mm O.D. (1.77 in.) and 30 mm I.D. (1.18 in.). The extrusion was then annealed at 700 - 750 C followed by a very slow cooling. This was only a softening anneal and not intended to improve corrosion resistance. However, because of the large amount of cold work, complete recrystallization occurred and during the slow cooling the beta zirconium phase decomposed into beta niobium and alpha zirconium. Without the slow cooling an unstable intermediate condition, the omega phase, could appear causing an even higher hardness.

The extrusion copper was removed in acid and the tubes were cold rolled by the Rockrite process. Three rolling steps were used with intermediate anneals of 700 - 750 C followed by slow cooling. The first reduction was 73%, the second 56% and the third 57%. The final dimension was 12 mm I.D. (0.473 in.) and 13.9 mm O.D. (0.548 in.). The final tube dimensions were obtained by drawing using molybdenum sulfide as a lubricant. Deformations up to 20% were obtained. The final anneal at 580 C could be given either before or after the drawing operation depending on the final use. The molybdenum sulfide lubricant was difficult to remove, but was successfully removed in a nitric-hydrofluoric-water bath followed by rinsing in a solution of $25\% \text{HNO}_3 + 25\% \text{C}_2\text{H}_5\text{OH} + 50\% \text{H}_2\text{O}_2 + 2 \text{ drops HF/100 cc.}$

An X-ray investigation of the orientation showed the extruded tubes to have a double fiber texture with $[10\bar{1}0]$ and $[11\bar{2}0]$ parallel to

the tube axis in which the $[10\bar{1}0]$ axis is predominant and with the hexagonal base plane laying parallel to the tube wall. The extruded texture is maintained by the first several cold rolling steps. However, the drawn tubes begin to show a ring fiber texture which is first implied in the third rolling step. An anneal at 575 - 750 C does not change this texture.

Mechanical testing these tubes showed that the extruded and rolled tubes have the same creep behavior as the extruded and swaged rods so that the results obtained for the extruded material can be applied to seamless tubes. The normal compression and expansion tests for Zircaloy-2 are completely fulfilled by the tubes made from the alloy $Zr + 3Nb + 1Sn$.

Corrosion tests to date show that after 1000 hours little if any difference exists between the normal rolled corrosion specimens and the fabricated tubes. However, when a poorer surface condition exists, then the corrosion drastically increases.

32)

Welding

The major difficulty in welding niobium containing alloys is the lower fluidity and the poor corrosion resistance of the cast welded structure. The alloy $Zr + 3Nb + 1Sn$ could be welded by either argon arc or electron beam welding processes and, with proper set-up, the weldability of these alloys was equally as good as for Zircaloy-2. Figure 27 shows the effect of niobium on the corrosion resistance in the welded material. In the non-heat treated condition the

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FIG. 4-27 CORROSION OF WELDED SAMPLES, CORRODED IN STEAM 400°C, 200 Atm, 14 DAYS.

corrosion attack increases with increasing niobium content. When the sheet is heat treated at 575 C the corrosion values return to those of the unwelded material. The corrosion resistance of the electron beam welded material was slightly poorer than the argon arc welded material, but the hydrogen pick-up during corrosion was less. This was due to either a wider heat affected zone or to the removal of some essential minor volatile impurity during the vacuum welding.

The use of a weld filler alloy $Zr + 0.5 Nb + 1Sn$ resulted in an improvement in the corrosion behavior of the as-welded material. In fact in the thicker material the corrosion values were almost the same as the material which was welded and heat treated. In the thinner material the improvement was not so evident. The slow cooling associated with the thicker material was probably responsible. Hydrogen pick-up in this material was found to be very high, but this could be associated with the longer time the weld zone was in the molten state, thus the weld acted as a "getter" for the atmosphere. This point is currently under further investigation.

Some reactor applications may require welding niobium containing alloy parts to Zircaloy-2. Corrosion testing these weldments showed that the as-welded structure had the same corrosion resistance as the Zircaloy-2 components and that no galvanic attack was observed between the two materials.

Both the tensile and yield strength of the welded specimens were higher than the original starting material and the ductility somewhat

lower. Material joined with a weld filler alloy was much improved in ductility while the tensile and yield strength values were only slightly reduced. In the normal welded material, the hardness values increased in the weld zone; in the material welded with the filler alloy the hardness showed little change across the weld seam; and in the niobium alloy-Zircaloy-2 welded couples the hardness values decreased from the high value for the niobium alloy to the lower value for Zircaloy-2.

39)

Elongation due to Thermal Cycling

Metals used as reactor construction components will be subjected to repeated thermal cycles due to changes in the reactor power level and to repeated reactor start-ups and shut-downs. Because zirconium has a hexagonal structure, there exists a strong anisotropy with the orientation. To investigate this problem, several lengths of $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ and Zircaloy-2 tubes were subjected up to 1000 thermal cycles between 20 and 350 C. There was a slight increase in the length of the tubes annealed between 575 and 1000 C. Thermal cycling cold drawn tubes led to a shrinkage of 0.05 - 0.1% at cold reductions of 20 - 27%. This is due to a relaxation process which was observed after the first thermal cycle. Thus, for the use of cold drawn tubes of these alloys it is advisable to thermal cycle at least once before loading with fuel or cutting to final size. There was no difference noted as to whether the testing took place in argon or in air. No change could be detected in the surface roughness with thermal cycling. No difference in the texture could be determined in either Zircaloy-2 or the $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ alloy. However, Zwicker⁴⁰⁾ found a

very heavy elongation in rolled and annealed tubes of Zircaloy-2 as shown in Figure 28. This difference was probably due to the sample size and heat treatment. Only the extruded material (shown by the open and closed circles) agreed with the above results. It is possible that this material behaved the same as titanium where the texture of the extruded and drawn materials are essentially the same.

VIII. Future Investigations

The next stage in our work is to irradiate the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ in a comparative study with Zircaloy-2. Contract negotiations are nearing completion between Metallgesellschaft AG, Euratom, and the Gesellschaft für Kernenergieverwertung in Schiffbau und Schifffahrt mbH. This contract will provide the opportunity to make a survey study on the effects of radiation damage. The swimming pool reactor operates at a power of 5 MW at a maximum flux of $3 \times 10^{13} \text{ n/cm}^2/\text{sec}$. Two exposures are planned, namely 3 and $8 \times 10^{19} \text{ n/cm}^2$. Comparative mechanical properties will be determined including tensile, impact and weld strength. Another set of tensile specimens will be irradiated in the highest fast flux region to be compared with a similar set irradiated in the lowest fast flux region to determine the effect of the fast/thermal flux ratio. Corrosion properties in a radiation field will be determined in specially designed static autoclaves as well as the tensile properties of corroded tensile specimens. Also, metallographic tests are planned to determine if radiation damage will increase the rate of decomposition of the beta zirconium into beta niobium and alpha zirconium.

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FIG. 4-28 INFLUENCE OF TEXTURE AND SPECIMEN FORM ON THE ELONGATION OF ZIRCALOY - 2 by Thermal Cycling. Sample Length 70 mm (2.755 in.). Lengths Determination at 21 °C.

IX. Summary

The zirconium-niobium phase diagram has been revised to take into account the effect of oxygen. Two diagrams have been prepared, one for 800 ppm oxygen the other for 200 ppm. Both of these diagrams show a eutectoid transformation temperature of 590 C and a three component system appears, extending the transformation interval over 200 C for the sponge alloys and 100 C for the iodide alloys. This is due to the ternary effect of the oxygen addition.

Ternary diagrams were determined for the zirconium-niobium-hydrogen system. Hydrogen as well as niobium lower the transformation temperature of zirconium. Over 300 ppm hydrogen causes stabilization of the beta zirconium phase at 540 C which could lead to a bad corrosion behavior.

Ternary diagrams were also determined for the system zirconium-niobium-tin. The solubility of tin in alpha zirconium was found to increase with increasing temperature in the range 590 to 700 C and the niobium solubility decreases. The equilibrium reaction in this temperature range is very sluggish.

A distinct dependence of the corrosion resistance on the structure was found. Material annealed below the $\alpha_{\text{Zr}} + \beta_{\text{Zr}}$ transformation range had good corrosion resistance associated with the presence of the β_{Nb} -phase, while the material annealed above transformation temperature of 590 C had very poor corrosion resistance associated with the β_{Zr} phase. The corrosion rate in non-heat treated material

increases with increasing niobium content. Palladium, chromium and molybdenum additions had either no effect or else were very harmful to corrosion resistance of the basic zirconium-niobium alloy. Tin additions were favorable, especially in the form of the alloy $\text{Zr} + 3\text{Nb} + 1\text{Sn}$.

The $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ alloy proved worthy for consideration as an alloy for reactor use. This alloy has corrosion properties equal to those of Zircaloy-2 and does not form the spalling corrosion product with increasing corrosion rate. The creep properties at 250 C are twice as good as those of Zircaloy-2 and the tensile properties likewise better. Hydrogen pick-up appears to be somewhat lower and, according to impact tests, has less effect on the strength of the $\text{Zr} + 3\text{Nb} + 1\text{Sn}$ alloy than Zircaloy-2. This alloy can be formed into tubes by extrusion to a thick wall tube, then cold rolling and drawing to final size. Welding presents no problem, however, the welds must be heat treated to insure good corrosion behavior. A low niobium filler alloy minimizes the bad corrosion effect on the non-heat-treated weld seams.

X. Acknowledgements

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RESEARCH ON ALPHA-ACTIVE EUTECTOID ZIRCONIUM ALLOYS

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The purpose of the research program in progress at Compagnie PECHINEY under Euratom sponsorship is, as a main goal, to develop a zirconium alloy possessing good mechanical properties over a temperature range from 300 up to 700°C.

Such an alloy must be tailored to meet the following requirements:

- to have good tensile and creep properties over the proposed temperature range;
- to be thermally stable, i.e. to retain sufficient ductility at room temperature after a long heating time, stressed or unstressed;
- to present, at room temperature or at moderately high temperature, enough plasticity to be fabricated into shapes as required by nuclear industry.

Furthermore, additional requirements or considerations must be taken into account in view of nuclear applications:

- acceptable cross-section;
- usable corrosion resistance in water or steam, tied to hydrogen absorption and embrittlement.

I - GENERAL SURVEY OF ZIRCONIUM ALLOYING BEHAVIOR

We have considered the various means to strengthen the zirconium matrix.

Among those, one can notice:

- a. addition of an alpha-phase stabilizing and hardening element;
- b. addition of a beta phase stabilizing and hardening element;
- c. addition of alphasgenic plus betagenic elements using only soft annealing heat-treatment for stabilization.

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These three kinds of alloys have already been extensively studied and new improvements, with regard to mechanical strength, are questionable.

- d. alloys containing alphagenic plus betagenic elements, where the strengthening effect is obtained from structural reactions from the beta phase. Heating in the alpha-beta or beta range, followed by rapid quench, with or without further tempering, promotes a mechanism of hardening analogous to that for titanium alloys. Zirconium containing a relatively large addition of a beta stabilizing element can be hardened by the following transformation:

beta (lean) $\rightarrow$ omega + beta (enriched) $\rightarrow$ alpha + beta (enriched).

Lean alloys, having insufficient alloy content to retain beta at room temperature are hardened by the following transformation:

beta (lean) $\rightarrow$ alpha prime $\rightarrow$ alpha + beta (enriched).

Simultaneously, the alpha-phase is hardened by suitable alphagenic elements.

This kind of alloys has been, and is still, the field of an extensive research effort, the betagenic elements being chosen among molybdenum, niobium, tantalum, etc, the alphagenic elements being chosen among tin, aluminum, etc.

- c. alloys in the range alpha + dispersed compound. The strengthening effect is obtained by alloying with an alpha-phase stabilizing and hardening element simultaneously with beta promoter elements giving compounds by eutectoid decomposition.

Other processes could be considered to get appreciable strengthening at elevated temperatures. For instance:

- f. dispersion throughout the matrix of a natural oxide-phase, formed by internal oxidation-reduction reactions, as used in S.A.P.
(Al + Al₂O₃) or in special sintered nickel-base pseudo-alloys
(Ni + ThO₂).
- g. artificially dispersed fine particles by mechanical addition, such as:
- oxides (Al₂O₃ - ThO₂ - MgO, etc.), nitrides, carbides, borides,

beryllides, etc.

- intermetallic compounds
- refractory metals (Mo-W).

h. reinforcement with continuous or discontinuous fibers, for instance metallic or non metallic fibers.

These three former possibilities are not to be neglected. But we have considered that this field is insufficiently improved up to now to give fruitful immediate applications.

On the other hand, the field of alpha + dispersed compound has been considered as a more promising one.

II - CONSIDERATIONS ABOUT ALPHA + COMPOUND ALLOYS

If we consider the ways of improvements in the field of high-strength titanium base alloys, we can see that, beside all alpha or all beta, or alpha-beta alloys with structural reactions, a new range of very interesting mechanical properties has been obtained from the alpha + compound alloys (1-2). We have therefore, thought that such a system could be a fruitful one in the case of zirconium base alloys. As we have already stated above, this kind of alloys may be termed "alpha dispersoid" alloys and are basically ternary or more complex alloy containing:

- one or more alloy addition which strengthens the alpha phase;
- one or more beta promoter addition (called active eutectoid), that is to say any addition which, after solid solution into the beta phase, can give rise to an active eutectoid decomposition reaction. The intermetallic compound, Zr-M, obtained in a such natural way, will act as an homogeneously and finely dispersed insoluble precipitate to strengthen the alpha matrix.

a. Choice of the betagenic element

The element to be considered must have a rather large solid solubility in the beta phase and must give, after solid solution heat treatment, an eutectoid decomposition sufficiently rapid (active) to be obtained either during cooling or following a rather short temper heat-treatment. Considering the various

equilibrium phase diagrams, the following observations can be presented:

1^o / Molybdenum - Niobium - Tantalum:

The positions of the eutectoid points are:

	<u>Mo</u>	<u>Nb</u>	<u>Ta</u>
T ^o C	780	600	720
% weight	7,5	18	7

But it is known (Ref. 3 to 8) that these elements, when present in sufficient amounts, stabilize strongly beta zirconium to room temperature during rapid cooling from the beta field. The decomposition beta → alpha + compound is very sluggish and not usable practically.

Furthermore, the eutectoid line in the Zr-Nb system is at rather low temperature, and any strengthening effect would disappear at this temperature and higher, since the compound is put into solid solution.

The addition of tantalum is undesirable because of its high thermal neutron cross section.

2^o / Copper

Copper is one of the alloying additions giving rise to the more interesting eutectoid reactions in the case of the titanium-base alloys.

In the case of Cu-Zr alloys, the eutectoid is at 1,6 % Cu - 822^oC.

Detailed studies, particularly in the United Kingdom, have been carried out on the effects of this alloying addition, and commercial or experimental alloys are now proposed such as binary Zr + 5 % Cu (Ref. 13) or Zr-Mo-Cu (Ref. 9 and 12) or Zr-Mo-Nb-Cu (Ref. 14). Some of these alloys present interesting mechanical properties in the temperature range 500-600^oC, due to heat-treatments giving rise to the eutectoid formation of the compound Zr₂Cu (Ref. 10).

Nevertheless it must be pointed out that very few investigations seem to have been undertaken in the field of zirconium base alloys containing both copper and some alpha-phase strengthener, with the exception of the Zr-Sn-Cu system (Ref. 15).

3⁰ / Chromium

The eutectoid takes place at 1,8 % - 835⁰C. The positive effect of chromium is also used in the same family of English alloys (Ref. 12) as above, with the possibility to initiate eutectoid reaction to improve the mechanical properties.

4⁰ / Other Elements

Among the other elements giving with zirconium a phase diagram of the eutectoid type, we can consider:

	<u>W</u>	<u>Ag</u>	<u>Co</u>	<u>Fe</u>	<u>Mn</u>	<u>V</u>	<u>Ni</u>
T ⁰ C	850	825	810	800	795	780	810
Weight %	0,8	3	3	2,5	3	5	1,3

A detailed examination of the behavior of these elements leads to the following summarized conclusions:

- tungsten gives an eutectoid at low amount, so that the effect would not be interesting. Also alloying with tungsten is particularly difficult;
- silver and cobalt could be useful, but special considerations must be kept in mind in view of nuclear use;
- iron does not give rise to an active eutectoid decomposition (Ref. 11);
- manganese is able to lead to an eutectoid decomposition which seems nevertheless very sluggish;
- vanadium appears to be very interesting. The amount required is moderately high. The position of the eutectoid line in temperature range gives hope that the strengthening effect due to the precipitate could be retained at rather high temperature;

- nickel can be also kept under consideration; the eutectoid line is at a high temperature. On the other hand, this element is, after copper, the most active in the field of titanium-base eutectoid alloys (Ref. 1). Its rather deleterious effect by hydrogen pick-up has been more or less proved. But, from this point of view, the effect of this element must be considered as entering into a complex alloy and in the form of a compound.

b. Choice of the alphagenic element

The elements which strengthen the zirconium alpha-phase are rather well known, as are their effects on mechanical properties and corrosion resistance, among others.

In the course of our research program, the first point to be considered will be the possible interaction of these elements with the betagenic element, which could change the kinetics of the eutectoid reactions obtained in the case of the binary systems, Zr + betagenic element.

III - OBTAINING A FINELY DISPERSED COMPOUND

The precipitation, or more exactly the tendency to the formation of a compound Zr-M with a suitable physical shape, finely and homogeneously dispersed throughout the matrix, is the basic phenomenon used in the concept of these alloys termed "alpha-dispersoid". Getting the suitable structure is dependent on two major factors:

- the prior thermal history of the alloy, and mainly the hot-working conditions;
- the type of heat treatment applied.

a. Hot working

There are four temperature regions in which this type of zirconium base alloys can be hot worked:

- the all-beta region
- the two phase alpha-beta region
- the three phase alpha-beta-compound region
- the two phase alpha-compound region.

Each of these regions lead to particular and different structures which in turn act directly on the response of the alloy to the further heat treatment. The hot working processes used in the fabrication of the alloy are therefore of considerable importance.

b. Heat-treatment

Based on the phase-diagrams, the usable heat-treatment can be performed in six different ways:

1^o / Alpha + compound region heat treatment:

This treatment, performed at a temperature below the eutectoid temperature, and followed by air or furnace cooling, will promote a structure consisting in an alpha matrix containing a dispersion of rather coarse compound particles. This case is not particularly interesting, due to the fact that it normally gives no hardening effect, but, on the contrary, a softer condition.

It must be noticed that the prior fabrication controls strongly the structure of this alpha-compound annealed alloy - in order to promote a random distribution of the compound, it is advisable to hot work in the alpha compound region, in order to break up the compound phase as it forms.

2^o / Alpha-beta heat treatment, followed by quench:

The alloy is heated to a point in the alpha-beta region, allowed to come to equilibrium and then quenched rapidly to room temperature; the beta phase will transform into martensitic alpha, or into very finely dispersed eutectoid structure, or both. Such a structure will give a considerably improved strength, with some loss of ductility. The ductility is mainly dependent on the size and shape of the alpha grains, which in turn, depends strongly upon the fabrication history. In order to get an uniformly fine equiaxed-alpha structure, it will be preferable to give the alloy a sufficient reduction in the

alpha-beta region.

3^o / Alpha-beta quench followed by temper heat-treatment

If the alloy, quenched from the alpha-beta region, is submitted to a tempering heat treatment carried out at a temperature below the eutectoid temperature, the effect will be:

- either to initiate the eutectoid decomposition, in the case of a poorly active-eutectoid alloy;
- or to promote decomposition of the martensitic alpha into alpha and compound and to spheroidize the fine alpha-compound eutectoid, if already formed during the quench.

In this later case, the strength is decreased while ductility is improved. Thus, it will be possible to adjust specifically time and temperature of this temper heat treatment in order to get a suitable combination of strength and ductility.

As above the previous hot-working history is of primary importance.

4^o / Beta heat-treatment followed by slow-cooling

If the alloy is treated to a temperature above the beta transus and slowly cooled through the transformation range, the structure will consist normally of a basket-weave alpha pattern surrounded by a coarse alpha-compound eutectoid structure, thus giving rather low strength and good ductility; in contrast to case 1^o /, this structure is not dependent upon the fabrication history and this can be an advantage.

5^o / Beta heat-treatment followed by rapid cooling

If the alloy is treated at a temperature above the beta transus for a sufficiently long time to obtain an all-beta structure and then quenched to room temperature, the final structure will consist of martensitic alpha (with a small amount of finely dispersed compound at most). A maximum strength will be attained, with probably rather poor ductility.

Furthermore, this heat treatment has the advantage of

being relatively independent of hot-working history, with some possible exception for grain size.

6°/ Beta quench followed by temper heat treatment

As in case 3°, an interesting compromise between strength and ductility can be tailored by a proper adjustment of time and temperature of the temper heat treatment performed at a temperature below the eutectoid temperature.

In summary, in order to get high mechanical properties, the alloy will be heat-treated in the alpha-beta or beta region and then rapidly quenched to room temperature. Considering now the problem of ductility, if necessary an improvement of ductility will be obtained by a further tempering heat-treatment, performed in the alpha + compound region. The time and temperature of tempering will be adjusted to lead to a suitable compromise between strength and ductility.

IV - RESEARCH PROGRAM

Based on the forgoing considerations, our research program to develop an alpha-dispersoid zirconium base alloy, is being performed along the following lines:

Phase I

Phase I is a study of a range of binary alloys containing various amounts of a betagenic element, in an attempt to single out two or three of the most favorable combinations of composition, transformation schedule and heat-treatment, giving improved strength with acceptable ductility from an eutectoid reaction.

- 1 - double vacuum melting of billets;
- 2 - fabrication by extrusion into bars, the not working temperature being controlled either in the alpha-beta or in the beta region;
- 3 - detailed study, by optical and electron micrography and by hardness measurements, of the structures obtained following a large range of heat-treatments;

4 - for the most interesting combinations:

4-1 measurements of the tensile properties, at elevated temperatures;

4-2 study of the thermal stability after long time of heating;

4-3 study of the corrosion resistance in water and vapor.

Phase II

The binary combinations thus selected will serve as a basis for more complex alloys by adding alphagenic elements.

These alloys will be fabricated as in Part I, and will be submitted to:

- 1 - detailed study of possible interaction of the alphagenic element upon the eutectoid reaction and re-design, if necessary, of the more suitable heat-treatment;
- 2 - for the more promising cases, detailed evaluation of tensile and creep properties at elevated temperature, thermal stability and corrosion resistance to water and vapor.

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DEVELOPMENT OF IMPROVED ZIRCONIUM
ALLOYS FOR USE IN SUPERHEATED
WATER AND STEAM

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ABSTRACT

The objectives of this study are development of zirconium-base alloys having corrosion resistance and strength superior to Zircaloy-2 in 680°F water and 750° - 900°F steam, or development of alloys having improved strength at elevated temperatures and corrosion resistance equivalent to Zircaloy-2.

Approximately 100 binary compositions were screened by corrosion testing in 680°F water and 750°F steam; selected compositions were exposed to 900°F steam. Data obtained from these studies indicated a number of highly promising bases for ternary alloy investigation. During the past year, corrosion studies on ternary alloys were carried out. On the basis of 4800-hour tests, a number of ternary materials initially satisfy the program objective for the 680°F water environment. These compositions are based on Zr-1Sb, Zr-1Cr, Zr-0.5Nb, and Zr-0.5Sn with small additions of Te, Ge, Cr, or Fe. Further, the hydrogen pickup characteristics of these alloys are improved over Zircaloy-2, but acceptability on this basis remains to be demonstrated by mechanical property evaluation. For 3000-hour tests in 750°F steam, the alloys Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe are superior to Zircaloy-2 on the basis of corrosion resistance and strength; however, hydrogen pickup properties are about the same as Zircaloy-2 which is considered excessively high. In 900°F steam, a few materials are greatly superior to Zircaloy-2 but weight gains are very high. Additional development of ternary alloys is in progress.

DEVELOPMENT OF IMPROVED ZIRCONIUM
ALLOYS FOR USE IN SUPERHEATED
WATER AND STEAM

I. INTRODUCTION

At the present operating temperature of pressurized water reactors (approximately 600°F), Zircaloy-2 meets most of the requirements for a fuel cladding material. In particular, corrosion data in 600°F water show that no breakaway or transition to linear corrosion occurs for times up to 500 days, ⁽¹⁾ and the strength of this material --though probably not as high as desired--is considered adequate. However, higher reactor temperatures would result in more efficient operation and provide cheaper nuclear power. At temperatures not much above 600°F, for example 680°F, Zircaloy-2 exhibits breakaway corrosion (nonprotective) after only 100 days' exposure; in steam at 750°F, transition to linear corrosion occurs in 40 days. These corrosion properties are considered unsatisfactory for use as cladding material at these higher operating temperatures; moreover, strength of Zircaloy-2 at these temperatures is marginal and, for certain fuel element designs, wholly inadequate. With the need for improved zirconium alloys apparent, this program has the objective of developing materials markedly superior to those currently available. Specifically, the alloys to be developed should possess exceptionally good corrosion resistance to 680°F water and 750° to 900°F steam and should exhibit improved strength at elevated temperatures. Materials having corrosion resistance equivalent to Zircaloy-2 with improved strength were also desired.

During the past decade, considerable research and development efforts were carried out on zirconium. However, the sudden success of Zircaloy seemed to have retarded progress in further zirconium alloy development or has, at least, caused a discursive attack on this subject. This observation is exemplified by the voluminous accumulation of data available on minor compositional variations of

Zircaloy or the effect of very dilute additions to zirconium on corrosion behavior. In more recent years, comparatively higher concentrations of alloying elements were employed in development programs. However, very few of these programs systematically investigated binary alloys which might then be used for development of ternary and quaternary compositions. As a result, corrosion data on binary compositions--other than for relatively dilute alloys--remain incomplete. Although some very promising compositions have resulted from past work, no significant improvements over Zircaloy were achieved for higher temperature reactor application.

In this program, a comparatively large-scale, binary alloy corrosion screening investigation was carried out in both 680°F water and 750°F steam; selected binary materials were also evaluated in 900°F steam. The results obtained from these investigations provided a number of bases from which ternary compositions could be prepared. This procedure has resulted in a number of ternary alloys which, on the basis of corrosion resistance, strength, and--in some cases--hydrogen pickup, initially satisfy the program objectives and are superior to Zircaloy-2.

II. SCOPE OF INVESTIGATION

The initial step was to learn of the work being conducted on zirconium alloy development at other organizations. This information has been summarized⁽²⁾ and was a guide in choice of binary compositions for evaluation. First, an intensive study on selected elements known to improve corrosion resistance in water or steam when present as relatively small additions was indicated. For this study, the following binary zirconium alloys were prepared:*

Zr-(0.5, 2, 5, 10, 20, 25, 30, 50, 75) Nb

Zr-(0.5, 1.5, 3, 5, 7, 10, 20) Sn

Zr-(0.25, 1, 3, 5, 9) V

Zr-(0.25, 1, 2.5, 4, 6, 10) Sb

* All compositions given in weight per cent.

Dilute niobium additions to zirconium have been shown⁽³⁾ to greatly enhance corrosion resistance (particularly in steam) and markedly improve hydrogen pickup properties. In Canada,⁽⁴⁾ alloys in the region of 2.5w/o Nb were studied, and this system was of considerable interest to various organizations. However, the main reason for investigation of high niobium-zirconium alloys was due to Russian work⁽⁵⁾ which showed a minimum in oxidation rate for alloys in the range 25-30w/o Nb and the possibility of acceptable corrosion resistance of such materials. Dilute alloys with tin are well known for enhanced corrosion behavior, but very little information was available on the properties of compositions with greater than about 4w/o Sn. The choice of vanadium and antimony alloys for study beyond the concentrations of 2a/o V and 4a/o Sb were based on reports from KAPL⁽⁶⁾ of promising compositions within these systems for specific water and steam media.

In addition to the above compositions, binary alloys prepared for evaluation in superheated water and steam were the following:

0.25, 1, 3, (each); Fe, Co, Ni, Cr, Cu,
W, Mo, Ta, Si, Ge,
Te, As, Bi, Pb, Pt,
Pd, Rh, Ag, Au

Some of these have not been previously studied, whereas others have been evaluated in small concentrations and have propitiously affected corrosion properties. The range of compositions for the screening program represents, in most cases, both low and comparatively high alloy concentrations.

The pickup of hydrogen by the alloy from the corrosion reaction was recognized as an important property of the material. Since the formation of platelet hydrides or massive grain boundary hydride can severely reduce the impact properties of zirconium, this factor could conceivably act as the eliminating parameter in an otherwise acceptable, corrosion-resistant alloy. Hydrogen pickup in a given medium is, among other things, a function of alloy composition; thus,

this third property must be added to corrosion resistance and strength as factors for evaluation. Since it would be nearly impossible to screen materials on the basis of all three parameters, corrosion resistance was considered the principal factor and evaluation was initially carried out on this basis. Acceptable materials were then tensile tested at elevated temperatures and the hydrogen pickup characteristics were determined. The resulting data were then used in planning of ternary compositions.

III. EXPERIMENTAL PROCEDURES

A high-quality sponge zirconium was used in preparation of alloys; the arc-melted hardness of this material was 112 VHN and the supplier's impurity analysis is shown in Table I. Niobium was obtained as high-purity, electron-beam melted sheet; the vanadium used was produced by the calcium-reduction process; and generally speaking, the alloying additions were of the highest purity readily obtainable. Alloys in the form of 100-gram "button" ingots were prepared by nonconsumable arc-melting under a positive pressure, high-purity argon atmosphere. To insure homogeneity, all specimens were turned over and remelted five times, and possible loss of constituents by volatilization or contamination by electrode or crucible material was checked by accurately weighing the specimens prior to and after melting. Alloys containing tungsten, molybdenum, tantalum, and niobium were prepared by first melting a Zr-50X master alloy.

The button ingots were sealed into low-carbon steel jackets by heliarc-welding for the purpose of avoiding air contamination during fabrication. Specimens were rolled at 1550°F taking a 10 per cent reduction per pass, and a relatively long heating time was allowed between passes. Binary alloys were finish-rolled below the transformation temperature for the purpose of obtaining a nearly similar microstructure, where phase equilibria allowed, in all specimens.

The techniques employed in preparing specimens for autoclave testing as well as actual testing procedures closely followed specifications outlined by Kass. ^(7, 8) Specimens were first milled to

TABLE I
SUPPLIER'S IMPURITY ANALYSIS
OF SPONGE ZIRCONIUM

Impurity	Concentration, ppm
Al	32
B	< 0.2
C	*
Cd	< 0.3
Co	< 5
Cr	30
Cu	20
Fe	150
H	*
Hf	55
Mg	170
Mn	15
Mo	10
N	20
Nb	*
Ni	<10
O	670
Pb	5
Si	30
Sn	< 5
Ta	*
Ti	<20
V	<20
W	<40
Zn	*

* Not available

remove any iron contamination and a bright, metallographic-type surface was obtained by lapping or hand polishing on emery papers followed by pickling and various rinsing and final etching procedures. In 680°F water and 750°F steam, static autoclave systems were used for corrosion testing; however, for 900°F steam, a replenished system was employed. To evaluate our autoclave systems, Zircaloy-2 sheet from Bettis Atomic Power Laboratory*--for which the corrosion properties in 680°F water and 750°F steam had been determined--was tested. The weight gain data agreed very well with that of Bettis.

IV. RESULTS AND DISCUSSION

Corrosion data on a multitude of alloys were obtained during this development program. For extensive and detailed coverage of all compositions, the reader is referred to the progress reports on this program.⁽⁹⁾ If a particular alloy is not mentioned in this discussion it can be assumed that the corrosion resistance was comparatively poor. Thus, the data will be presented in sequence of alloy development for a particular medium.

A. 680°F Water

All of the binary alloys previously mentioned were exposed to 680°F water; after various exposure times, the weight gain of each specimen was determined. Some specimens showed extremely high weight gains or severe spalling and white oxide formation (nonprotective) after only 7 days' exposure. Some of the compositions which showed such behavior were Zr-(50, 75) Nb, Zr-12Sn, Zr-(3, 5, 9) V, Zr-10Sb, Zr-(1, 3) Ta, Zr-(1, 3) Bi, Zr-(0.25, 3) Ag, Zr-1Au, and Zr-3 (W, Mo, Te, Ge, Pb, Rh, Pd). These specimens were not further evaluated in this medium, and at various other exposure times additional specimens were also determined to have poor corrosion resistance to 680°F water.

* The authors express their thanks to E. Hillner and W. W. Kirk for providing this material and for their suggestions on testing procedure.

Exposure of a number of alloys was continued to 101 days; the corrosion behavior of selected compositions is shown in Figures 1, 2, and 3. Zircaloy-2 exhibited breakaway corrosion after 80 days' exposure at a weight gain of 30 mg/dm^2 which is a shorter time than determined by Bettis; only one point, however, represents post-transition corrosion so the slope is not accurately defined. The behavior of niobium-containing alloys (Figure 1) is such that corrosion resistance decreases with higher alloying concentrations. The Zr-0.5Nb alloy shows excellent corrosion properties, which was known from past work, but higher contents of niobium resulted in higher weight gains. Interestingly, there is apparently an absence of breakaway corrosion in the Zr-2Nb and Zr-30Nb alloys--at least for 45 days' exposure--even with the formation of relatively heavy oxide coatings. The Zr-0.5Sn composition showed good corrosion resistance to 680°F water, but Zr-1.5Sn experienced a sharp transition to accelerated corrosion after 45 days' exposure. The dilute zirconium-vanadium binary alloys (Figure 2) exhibited transition before Zircaloy-2 and, as previously mentioned, higher compositions showed very poor corrosion resistance to this medium. The Zr-1Sb alloy exhibited the desired black, lustrous oxide coating; however, the composition Zr-0.25Sb showed a light gray, heavy, apparently nonprotective coating; higher contents of antimony resulted in poor corrosion properties. The low concentration zirconium-iron composition had good corrosion resistance, but Zr-1Fe and Zr-3Fe exhibited transition before Zircaloy-2. Figure 3 shows additional materials which, with the exception of Zr-1Co, indicated acceptable corrosion properties. In particular, Zr-0.25Te, Zr-0.25Mo, and Zr-1Cr showed the desired corrosion resistance; the Zr-3Cr material did not exhibit good resistance to 680°F water.

A report⁽¹⁰⁾ on the effect of 0.5 and 2.0a/o additions of a number of elements to zirconium showed that germanium, tellurium, silicon, niobium, antimony, and yttrium are--in that order--the most potent solid solution strengtheners. These results, in conjunction with data obtained from the corrosion screening tests, allowed for choice of binary base compositions for preparation of ternary alloys and indicated certain third component additions. These bases, the minor alloying addition, and the ternary alloys prepared are presented in Table II.

FIG. 6-1 CORROSION PROPERTIES OF SELECTED BINARY ZIRCONIUM ALLOYS IN 680°F WATER.

FIG. 6-2 CORROSION PROPERTIES OF SELECTED BINARY ZIRCONIUM ALLOYS IN 680°F WATER.

FIG. 3 - CORROSION PROPERTIES OF SELECTED BINARY ZIRCONIUM ALLOYS IN 680°F WATER,

TABLE II

ALLOY BASES, MINOR ADDITIONS, AND TERNARY COMPOSITIONS
RESULTING FROM BINARY ALLOY CORROSION
STUDIES IN 680°F WATER

Zr-1Sb

Zr-1Cr

Zr-0.5Nb

Zr-0.5Sn

Zr-0.25 (Fe, Cr, Mo, Cu, Te, Ge)

Zr-1Cr-1Sb

Zr-1Cr-0.5(Nb, Sn)

Zr-1Cr-0.25(Fe, Mo, Cu, Te, Ge)

Zr-1Sb-0.5(Nb, Sn)

Zr-1Sb-0.25(Fe, Cr, Mo, Cu, Te, Ge)

Zr-0.5(Nb, Sn)-0.25(Fe, Cr, Mo, Cu, Te, Ge)

Corrosion evaluation of these materials was carried out in 680°F water for a total time of 200 days. In no case was rapid, catastrophic corrosion experienced as in many of the binary alloys previously mentioned. While many of the compositions had undesirable corrosion properties in this medium, a number of very promising alloys were obtained which are more corrosion-resistant than Zircaloy-2. The curves shown in Figure 4 and Figure 5 represent the corrosion behavior of selected materials which are considered highly promising. In Figures 4 and 5, for example, the alloys Zr-1Cr-0.25Te, Zr-1Sb-0.5Te, Zr-0.5Nb-0.25Te and Zr-0.5Sn-0.25Ge do not exhibit transition to a linear corrosion rate up to 200 days' exposure, whereas Zircaloy-2 shows transition after about 85 days' exposure in these tests. The other compositions represented in these figures are at least equivalent to Zircaloy-2 in corrosion resistance to 680°F water. Moreover, Zircaloy-2 shows a small amount of white, nonadherent oxide, whereas these experimental alloys exhibited adherent coatings. While the post-transition corrosion rate of Zircaloy-2 appears well defined, the linear portion of the curves for Zr-1Sb-0.25Ge and Zr-0.5Sn-0.25Te are determined by only a single point, and an accurate comparison is difficult. If one applied the assumption that the linear portion can be extrapolated to zero, then these experimental alloys would have a lower breakaway corrosion rate than Zircaloy-2. The validity of this extrapolation is, however, questionable.

It is interesting to note that four of the above promising compositions contain a small tellurium addition. As pointed out by Bibb et al.,⁽¹⁰⁾ there is a possibility that tellurium can exist in the oxide film in a higher valence state (+5) than zirconium (+4)--thus contributing electrons to the oxide film and decreasing anion vacancies. Applying this assumption to the corrosion mechanism proposed by Chirigos and Thomas,⁽¹¹⁾ which visualized the rate-controlling process as the diffusion of anion vacancies or anions through the ZrO_2 film, they found that Zr-0.5a/o Te had very good corrosion resistance to 680°F water and 750°F steam. While factors other than valence state can also be applied to this mechanism, the results obtained with tellurium additions as a ternary component tend to confirm the binary alloy work of Bibb et al.

FIG. 4 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 680°F WATER.

FIG. 5 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 680°F WATER.

From the standpoint of corrosion resistance to 680°F water, the behavior of alloys represented in Figures 4 and 5 indicates definite promise and, in some cases, definite superiority over Zircaloy-2. A further requirement of an acceptable alloy is improved elevated temperature strength. Moreover, it is known that Zircaloy-2 absorbs between 30 and 50 per cent of the hydrogen liberated in the corrosion reaction, which results in a severe reduction of impact resistance. The determinations of hydrogen pickup characteristics and tensile strength of these ternary alloys are summarized in Table III.

The results obtained for Zircaloy-2 are in general agreement with various data available in the literature. It is known⁽¹²⁾ that the hydrogen pickup characteristics of Zircaloy-2 follow closely the weight gain curve due to oxygen absorption and oxide formation; thus, the total quantity of hydrogen present in the alloy depends on what stage of corrosion has been reached. Since Zircaloy-2 is well past transition at 200 days' exposure, the hydrogen content is very high; at the same time, the percentage absorbed is also very high. Compared to Zircaloy-2, the experimental alloys are greatly improved in hydrogen pickup characteristics--both in terms of total hydrogen absorbed in a given exposure time and in the fraction picked up. The improvement is due to the absence of nickel, which is known⁽¹³⁾ to cause severe hydrogen absorption during corrosion, and perhaps iron.⁽¹⁴⁾ However, the acceptability of even these magnitudes of hydrogen in zirconium remains questionable, for it is known that--under certain conditions--as little as 25 ppm hydrogen can cause reduced impact properties. Certainly the hydride morphology is also an important factor; it has been shown⁽³⁾ that spheroidal hydrides, accomplished by means of heat treatment, have a lesser effect on impact properties than the normal platelet-shaped hydride. Thus, while initial hydrogen absorption evaluation of these experimental alloys indicates improved materials, considerably more investigation on this aspect of corrosion is necessary.

TABLE III
HYDROGEN PICKUP PROPERTIES AND TENSILE STRENGTH
OF SELECTED TERNARY ZIRCONIUM ALLOYS AT 680° F

Composition, w/o	Hydrogen Pickup (680° F Water, 200 Days)			UTS (680° F), psi
	Weight Gain, mg/dm ²	Total H ₂ , ppm	Pickup Fraction, %	
Zircaloy-2	68.47	183	46	27,800
Zr-1Cr-0.25Te	35.79	54	15	32,800
Zr-1Sb-0.5Nb	68.59	63	12	--
Zr-1Sb-0.25Te	49.66	62	17	30,300
Zr-1Sb-0.25Ge	52.85	38	8	32,700
Zr-0.5Sn-0.25Ge	36.98	51	18	25,100
Zr-0.5Sn-0.25Te	42.84	55	18	30,200
Zr-0.5Nb-0.25Te	46.88	65	22	30,700

The ultimate tensile strength values presented in Table III also indicate an improvement over Zircaloy-2. As previously stated, tellurium and germanium are powerful strengtheners of zirconium. Thus, only 0.25w/o Ge or Te in combination with 0.5 or 1w/o of another element used here apparently strengthens zirconium above that of Zircaloy-2. The potent strengthening effect of tellurium can be seen by comparing the Zr-0.5Sn-0.25Te alloy with Zircaloy-2 containing nominally 1.5w/o Sn; the strength at 680°F of the experimental composition is higher than Zircaloy-2. The reasons why the same behavior should not be observed for Zr-0.5Sn-0.25Ge are unknown.

Since tellurium and germanium, in low concentrations, strengthen zirconium and impart good corrosion properties, it follows that optimum alloys of Zr-Sn-(Te, Ge), Zr-Sb-(Te, Ge) and others could be designed. Work in this area has been initiated, and the compositions prepared for evaluation are given in Table IV; at present, however, corrosion data on these materials are not available.

B. 750°F Steam

For development of zirconium alloys for use in 750°F steam, an approach identical to that described for 680°F water was employed. The binary compositions previously listed were evaluated in 750°F steam (1500 psi) for an exposure time of 34 days; the corrosion behavior of selected alloys, compared to Zircaloy-2, is presented in Figures 6 and 7. For this exposure time, the point representing the weight gain of Zircaloy-2 is actually in the breakaway portion of the corrosion curve.⁽¹⁾ Although the exposure time is too short for an accurate determination of corrosion behavior, the data are adequate for initial comparison with Zircaloy-2. Of particular interest is the corrosion resistance of Zr-3Cr; this composition was better than Zr-0.25Cr or Zr-1Cr, and because of the high alloy content good elevated temperature strength is possible. The Zr-1V alloy, which was very poor for water corrosion resistance, shows reasonably good properties in steam--as first pointed out at KAPL.⁽⁶⁾ Tellurium was an acceptable addition for steam, as well as for water; however, germanium additions resulted in "catastrophic" corrosion in this medium. Zr-0.25Mo exhibited

TABLE IV

TERNARY COMPOSITIONS PREPARED
FOR EVALUATION IN 680° F WATER

Zr-(0.4-0.9) Sn - (0.25-0.5) Te
Zr-(0.5-0.9) Sn - (0.25-0.4) Ge
Zr-(0.75-1.5) Sb - (0.2-0.4) Ge
Zr-(0.75-1.2) Sb - (0.15-0.4) Te
Zr-(0.75-1) Sb - (0.35-0.5) Nb
Zr-(0.75-0.85) Cr - (0.25-0.5) Te
Zr-(0.3-0.75) Nb - (0.25-0.5) Te

FIG. 6 - CORROSION PROPERTIES OF SELECTED BINARY ALLOYS IN 750°F STEAM.

FIG. 7 - CORROSION PROPERTIES OF SELECTED BINARY ALLOYS IN 750°F STEAM.

excellent corrosion behavior, but higher concentrations resulted in rapid weight gain. The high niobium, tin, vanadium, and antimony binary alloys all exhibited very high weight gains or severe white oxide formation with concomitant spalling.

From these investigations, a number of binary compositions were chosen as bases and minor additions for preparation of ternary alloys. The materials used and the range of ternary alloy concentrations studied are presented in Table V. Of the binary alloys evaluated in this medium, those shown in Table V were considered the most promising from the standpoint of corrosion resistance, potential strength, and anticipated hydrogen pickup properties.

Evaluation of ternary alloys in 750°F steam was carried out for 125 days; the behavior of selected materials, considered to be promising for steam application, is represented by the curves in Figure 8 and Figure 9. The curve for Zircaloy-2 agrees very well with previous work⁽¹⁾ for both the transition point and the post-transition corrosion rate. The alloys Zr-1Fe with 0.25 (Cr, Te) or 0.5Nb and Zr-0.5Nb-0.25Te do not exhibit breakaway corrosion up to 125 days' exposure. For the alloys Zr-3Cr-1Fe, 0.25Te and perhaps Zr-1V-1Fe the time to transition is about three times greater than Zircaloy-2. Only a single point represents the post-transition corrosion rate, so a meaningful comparison with Zircaloy-2 is not entirely possible; nevertheless, these compositions represent a significant improvement in corrosion resistance to 750°F steam.

The corrosion-hydrogen absorption characteristics of these alloys were determined as well as the tensile strength at 750°F; the results are summarized in Table VI. Except for the Zr-0.5Nb-0.25(Cr, Te) alloys, these materials show little if any improvement over Zircaloy-2 with regard to corrosion hydrogen uptake. If however, comparison with Zircaloy-2 is made on the basis of total hydrogen content only, then additional materials would have to be considered superior from the corrosion hydrogen absorption standpoint. In particular, Zr-1Fe-0.25Cr, Zr-3Cr-(0.25Te, 1Fe), and Zr-1V-1Fe would be judged as improved materials.

TABLE V

ALLOY BASES, MINOR ADDITIONS, AND TERNARY COMPOSITIONS
RESULTING FROM BINARY ALLOY
CORROSION STUDIES IN 750°F STEAM

Zr-3Cr
Zr-1V
Zr-1Fe
Zr-1Sb
Zr-0.5Nb
Zr-0.25(Cr, Mo, Te)
Zr-3Cr-1(V, Fe, Sb)
Zr-3Cr-0.5Nb
Zr-3Cr-0.25(Mo, Te)
Zr-1V-1(Fe, Sb)
Zr-1V-0.5Nb
Zr-1V-0.25(Cr, Mo, Te)
Zr-1Fe-1Sb
Zr-1Fe-0.5Nb
Zr-1Fe-0.25(Cr, Mo, Te)
Zr-1Sb-0.5Nb
Zr-1Sb-0.25(Cr, Mo, Te)
Zr-0.5Nb-0.25(Cr, Mo, Te)

FIG. 8 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 750°F STEAM.

FIG. 9 - CORROSION BEHAVIOR OF PROMISING TERNARY ZIRCONIUM ALLOYS IN 750°F STEAM

TABLE VI
HYDROGEN PICKUP PROPERTIES AND TENSILE STRENGTH
OF SELECTED TERNARY ZIRCONIUM ALLOYS
AT 750° F

Composition, w/o	Hydrogen Pickup (750° F Steam, 125 Days)			UTS (750° F) psi
	Weight Gain, mg/dm ²	Total H ₂ , ppm	Pickup Fraction, %	
Zircaloy-2	87.96	256	50	26,500
Zr-1Fe-0.25Cr	51.81	126	55	24,800
Zr-1Fe-0.25Te	68.84	204	71	22,300
Zr-1Fe-0.5Nb	88.60	212	58	30,200
Zr-1V-1Fe	72.00	163	50	31,800
Zr-3Cr-1Fe	65.43	158	50	30,000
Zr-3Cr-0.25Te	67.03	141	43	32,700
Zr-0.5Nb-0.25Cr	97.47	79	13	27,900
Zr-0.5Nb-0.25Te	66.95	94	30	27,200

But the total quantity of hydrogen and the pickup fractions are generally high, and such quantities of hydrogen in zirconium cause severe impact embrittlement. On the basis of hydrogen pickup properties, the acceptability of these alloys is doubtful--which is one factor other than corrosion resistance that limits the usefulness of Zircaloy-2. The ternary alloys of niobium with 0.25w/o Cr or Te, however, show reasonably good hydrogen absorption properties and these levels could probably be tolerated. The corrosion resistance of Zr-0.5Nb-0.25Cr is not, however, particularly better than Zircaloy-2, and strength is about the same. Perhaps the only alloy considered initially successful for 750°F steam application is Zr-0.5Nb-0.25Te, but the strength is about the same as Zircaloy-2 which is somewhat inadequate at this temperature. Notable strength improvements were obtained in the alloys Zr-1V-1Fe, Zr-3Cr-1Fe, 0.25Te, and Zr-1Fe-0.5Nb.

While some of these materials are considered promising from the standpoint of corrosion resistance, there is certainly the necessity for further improvement of this property as well as strength and hydrogen pickup properties. As in the case for alloys in 680°F water, an additional group of materials are being prepared to determine the compositions showing optimum corrosion and strength properties. These materials are given in Table VII. Unfortunately, no significant improvement in hydrogen absorption properties are anticipated--with perhaps the exceptions of alloys with niobium. With a lower corrosion rate, however, the total hydrogen content would be reduced for a given exposure time and the same pickup fraction.

C. 900°F Steam

A similar procedure was followed in development of alloys for corrosion resistance to 900°F steam; however, only a limited number of binary compositions were initially evaluated. The results of this investigation are given in Table VIII. The materials were exposed for 97 hours in a replenished autoclave system. Very few alloys are considered to exhibit promising corrosion resistance; however, notable improvements over Zircaloy-2 are apparent. In particular, Zr-0.5Nb, Zr-1V, Zr-3Cr, and Zr-(0.25, 1) Mo did not show evidence of break-away and had an adherent, lustrous oxide coating. Although these alloys

TABLE VII

TERNARY ALLOYS FOR DETERMINATION OF CONCENTRATIONS
SHOWING OPTIMUM 750°F STEAM CORROSION
AND STRENGTH PROPERTIES

Zr-(0.5-4)Cr-(0.5-2)Fe
Zr-(2.5-5)Cr-(0.25-1.5)Te
Zr-(0.75-2)V-(0.5-2)Fe
Zr-(0.4-0.9)Nb-(0.35-0.5)Te
Zr-(0.7Fe-1.2)Fe-(0.3-0.7)Te
Zr-(0.5-0.75)Nb-(0.4-0.6)Cr
Zr-(0.75-1.5)Fe-(0.35-0.5)Nb

TABLE VIII

CORROSION OF SELECTED BINARY ALLOYS
EXPOSED TO 900°F STEAM FOR 97 HOURS

<u>Composition, w/o</u>	<u>Weight Gain, mg/dm²</u>
Zircaloy-2	disintegrated
Zr-0.5Nb	65.05
Zr-2Nb	111.40 (no breakaway)
Zr-30Nb	264.40 (no breakaway)
Zr-(7, 10, 12)Sn	disintegrated
Zr-0.25V	disintegrated
Zr-1V	69.05
Zr-(3, 5, 9)V	disintegrated
Zr-Sb	disintegrated
Zr-(0.25, 1)Cr	disintegrated
Zr-3Cr	51.87
Zr-(0.25, 1, 3)Fe	high; improved as Fe content increased
Zr-0.25Mo	54.29
Zr-1Mo	58.78
Zr-3Mo	246.31 (no breakaway)
Zr-(0.25, 1, 3)Co, Pd	high weight gains, some whitening in certain specimens
Zr-0.25Ni	disintegrated
Zr-(1, 3)Ni	high weight gains, some whitening

are greatly improved over Zircaloy-2, they are, nevertheless, unacceptable from the standpoint of corrosion resistance due to the very rapid rate of corrosion.

In an attempt to further enhance corrosion properties, a number of ternary alloys were prepared from the above binary materials. The corrosion properties of a few selected materials which show at least some evidence of potential acceptability are represented in Figure 10. One notes that for an exposure time of 300 hours, no transition to accelerated, catastrophic corrosion was experienced as in the case for Zircaloy-2 after very short exposure times. Further, the addition of 0.25w/o Mo apparently improved the corrosion resistance of Zr-0.5Nb and Zr-1V, but such was not the case for Zr-3Cr. The addition of 0.5w/o Nb to Zr-3Cr and Zr-1Mo did not result in breakaway; however, the corrosion resistance was diminished by this addition. Since the corrosion properties of these alloys still are considered unacceptable, no evaluation of hydrogen pickup or tensile strength was warranted. Additional studies are being performed on a further group of alloys for potential use in this medium; the compositions shown in Figure 10 are being modified and further investigation of binary, high-chromium and high-iron alloys will be carried out.

V. SUMMARY

This program is concerned with development of zirconium-base alloys having corrosion resistance and strength superior to Zircaloy-2 and/or development of materials of equivalent corrosion resistance but exhibiting enhanced strength. The approach employed in the development effort has been an extensive binary alloy corrosion evaluation in superheated water and steam followed by preparation of ternary materials based on the former studies. At present, a number of ternary compositions have been developed for service in 680°F water which initially meet the objectives of this program on the basis of corrosion resistance, strength, and possibly hydrogen pickup. The ternary alloys based on Zr-1Sb, Zr-1Cr, Zr-0.5Nb, and Zr-0.5Sn with small additions of Te, Ge, Cr, or Fe are initially successful for 680°F water applications. In 750°F steam, Zr-3Cr-1Fe, Zr-3Cr-0.25Te, and Zr-1V-1Fe are the salient materials; on the basis of corrosion resistance and strength, these compositions are better than

FIG. 6-10 CORROSION PROPERTIES OF SELECTED TERNARY ALLOYS IN 900°F STEAM.

Zircaloy-2. However, the hydrogen pickup properties are about the same as Zircaloy-2, and the acceptability of this magnitude of corrosion-hydrogen absorption remains questionable. In 900°F steam, the corrosion properties of certain experimental alloys are greatly superior to Zircaloy-2, however weight gains are excessively high. Further work is being carried out on additional ternary alloys in 680°F water and 750°F steam for the purpose of obtaining compositions showing optimum properties; additional studies are planned for alloys in 900°F steam.

VI. ACKNOWLEDGMENT

The efforts of W. L. Ross in preparation of specimens, fabrication, and corrosion testing are gratefully acknowledged as well as the many helpful discussions with R. J. Van Thyne who acted as supervisor at the beginning of the program. This investigation is supported by the U.S./EURATOM Program and is administered by the Atomic Energy Commission under Contract No. AT(11-1)-578, Project Agreement No. 1; their support is greatly appreciated.

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CORROSION RESISTANCE OF IMPROVED ZIRCONIUM ALLOYS
IN HIGH TEMPERATURE STEAM

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Corrosion Resistance of Improved Zirconium Alloys
in High Temperature Steam

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1. Introduction

Today, there exist some reasonably good Zirconium alloys for the use in water-cooled reactors (Zircaloy-2 and -4) and in CO₂-cooled reactors (the "ATR" alloy and some similar Zr-Cu base alloys). But for applications in high-temperature steam (above 400°C), there is no standard Zirconium alloy available yet which could be considered satisfactory and well-proven. Zircaloy-2, for instance, has very poor corrosion characteristics at steam-temperatures above 350°C.

Since about four years, some promising development work on Zr alloys for superheated steam cooled reactors is in progress in several countries¹⁾⁻¹⁶⁾. From the literature we estimate that about 300 different alloys are being examined and evaluated for applications in high-temperature steam. A considerable part of these alloys is based on the system Zr-Nb.

In our reactor materials laboratory we are investigating the corrosion behavior of several Zr alloys in superheated steam. The experiments which started three years ago are now comprising 114 alloy compositions. Of course, within the restricted time-schedule of this symposium I can only present some of the results we got up to now.

2. Experimental

All alloys - besides Zircaloy-2 which was included for comparison purposes - were double Argon-melted (200 mm Hg pressure) in a tungsten-electrode arc-furnace. Only reactor grade Zr-sponge was used for the alloys (chemical analysis see table I). Generally, 300 gram batches were melted into a water-cooled copper crucible (60 mm diameter). The flat ingots were machined and hot rolled at 800°C to a thickness of 4 mm. The hot-rolled plates were mechanically descaled, annealed and subsequently cold-rolled. Annealing before cold-rolling and in between the cold-rolling steps was done at 650°C in vacuum (10^{-5} mm Hg). After a final step of 50% cold rolling 0.7 mm thick strips were reached.*) From these strips samples of the size 20 x 12 mm were cut.

All of the alloys were examined in the cold-worked condition, part of the alloys also in the recrystallized condition (15 min 700°C vacuum/furnace cooled) and in the β -annealed condition (10 min 1000°C vacuum/air cooled in evacuated tube). Since the cold-worked condition turned out to be most favorable corrosionwise, we shall restrict our presentation to this state.

Before initial weighing, the samples were pickled in a standard Zircaloy pickling-solution (HNO_3 -HF- H_2O); the depth of pickling was 20 to 25 μ .

*) Melting and fabrication of the alloys was done by Vacuumschmelze A.G. (subsidiary company of Siemens-Schuckertwerke A.G.)

Table I

Chemical Analysis of Zirconium sponge

(all figures in ppm)

Al	40	Mn	40
B	0.3	Ni	< 30
Cl	55	Si	50
Cr	102	Ti	30
Co	< 5	V	20
Hf	80	C	80
Fe	427	O	830
Pb	< 30	H	30
Mg	30	N	12

Brinell hardness (3000 kg, 10 mm ball):

112 kg/mm²

Our corrosion-experiments generally run at 500°C, to a limited extent also at 400 and 600°C. Most corrosion-tests were performed at atmospheric pressure, some others in micro-autoclaves at 300 at. The experiments at atmospheric pressure to which we will restrict our considerations were carried out in closed loops. The schematic design is shown in fig.1. The system works with an electrically heated and controlled superheater section. To eliminate any air contamination, purified Argon was injected continuously. Part of the alloys were also investigated in steam with the addition of hydrogen (1/100 atm partial pressure). The results of this particular study were presented elsewhere¹⁸⁾.

The specimens were weighed after 1, 2, 4, 8 ... days and subsequently inserted into the loops again. The weight gain data of each alloy are averaged from 3 or 4 samples. In every run we included, for comparison and control purposes, some samples of a large batch of vacuum-melted Zircaloy-2 and of argon-melted Zr-1%Nb. By these means we had a reasonably reliable control of any irregularities between the different test-loops and individual runs, which might be due to some temperature oscillations within the accuracy range of the equipments used. We consider the use of such control samples quite necessary at the temperature of 500°C, since already variations of $\pm 5^{\circ}\text{C}$ may influence the corrosion rates at a remarkable extent.

The samples were taken off after the first appearance of oxide-spalling. The longest exposure-time amounts now up to about 7000 hours.

Besides the weight gain we examined the metallographic structure of the oxide layers, the rates of hydrogen

FIG. 7-1.

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High-temperature steam corrosion-loop (1 atm.)

GI
615 820e

pick-up, the hydride formation and the embrittlement during corrosion. The relation between the precipitation of hydride and the mechanical properties is subject of a US/Eu-ratom contract (no. 024-61-RDA); this work will be presented elsewhere ¹⁹⁾.

3. Results and Discussion

3.1 Corrosion rates

A selection of corrosion data is presented in the fig. 2 - 8. The corrosion data plotted in one figure always stem from the same test run or from runs with good agreement between the corrosion rates of the control samples.

Fig. 2 shows a comparison between Zircaloy-2, Zircaloy-4, and some binary Zr-Nb alloys with 0.5, 1, and 2.5% Nb. I should mention that the data of Zircaloy-2 and Zircaloy-4 are not precisely comparable due to different melting procedure. Another run we made to compare both alloys in Argon-melted quality showed no significant difference between these alloys, whereas Ni-free Zircaloy-2 (with unbalanced Fe content) showed a considerably higher corrosion rate.

Among the binary Zr-Nb alloys the one with 0.5% Nb has the lowest corrosion rate. Increasing the Nb-content to 1% impairs the corrosion resistance, further increasing to 2.5% improves it again. With Nb contents above 5% the corrosion rates go up quite rapidly as was shown previously ¹⁸⁾.

In figure 3 we see the influence of some ternary additions to the Zr-0.5% Nb alloy. Only part of the ter-

FIG. 7-2.

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Corrosion of Zr alloys in steam at 500°C, 1atm

*G1
625770e*

FIG. 7-3

SIEMENS

Corrosion of Zr alloys in steam at 500°C, 1atm

GI
625775e

FIG. 7-4.

Corrosion of Zr alloys in steam at 500°C, 1atm

SIEMENS

Gl
625771e

FIG. 7-5

SIEMENS

Corrosion of Zr alloys in steam at 500°C, 1atm

GI
625772e

FIG. 7-6.

FIG. 7-7.

FIG. 7-8.

SIEMENS

Corrosion of Zr alloys in steam at 500°C, 1 atm

Gl
625768e

nary elements we examined are included in the plott. Remarkable improvements of the corrosion characteristics were reached by alloying Cu, Mo, Ni. The curves represent the ternary alloys with the most effective concentration level (most elements were added at the levels 0.1, 0.5 and 1 weight percent). I should like to mention here that the effectiveness of some ternary elements depends very strongly on the concentration. For instance, the alloy Zr-0.5%Nb-0.5%Cu shows lower corrosion resistance than the binary 0.5%Nb alloy.

Figure 4 demonstrates the effect of ternary elements to Zr-1%Nb and Zr-2.5%Nb. Still more pronounced than with the 0.5%Nb alloy, there are very strong improvements of the Zr-1%Nb alloys by additions of Cu, Mo, Ni; as previous investigations showed ¹⁸⁾, also Fe, Cr and V have a considerable beneficial effect in the range of 0.5%.

Contrary to that, we found only few possibilities to improve the 2.5%Nb alloy by ternary additions, although the binary alloy with 2.5% Nb behaves better than the one with 1%. Most elements even impaired the corrosion resistance. Therefore, we concentrated our further development work mainly to Nb-contents of 0.5 and 1% by weight. As we already mentioned, Cu looked particularly promising as a ternary addition. This is in agreement with recently published data of B.Cox et al.¹²⁾ and S.B.Dalgaard¹³⁾.

Besides Cu, another element was found to be very attractive as addition to Zr-Nb base alloys, namely Ca. In the literature, we know only one paper in which the effect of Ca upon the properties of Zr is studied, that is a report of H.H.Klepfer⁴⁾ who investigated in

his very extensive Zr alloy development work a binary Zr-Ca alloy with 1% Ca. This alloy, however, had an extremely high corrosion weight gain; it was about the worst of all the many alloys which Klepfer tested in high-temperature steam. Obviously it is not possible with Zr alloys to conclude from the effect of alloying elements in binary Zr alloys to that in ternary or more complex alloys. Therefore the value of studying binary Zr alloys as a screening test for the development of advanced ternary or more complex alloys is limited.

Figure 5 demonstrates the pronounced beneficial effect of ternary additions of Ca and Cu to Zr-Nb alloys. Please notice the relatively high corrosion rates of the binary Zr-Nb control samples. The yellow curves represent ternary Zr-Nb-Ca alloys; the red ones ternary Zr-Nb-Cu alloys. The least pronounced effect has been stated by addition of Cu or Ca to Zr-2.5%Nb. Nevertheless it is interesting to note that, with this basic type, the Ca-bearing alloy has better corrosion resistance than the alloy with 0.5% Cu, which independently was studied by S.B.Dalgaard¹³⁾.

I should now like to draw your attention to the high sensitivity of Ca-additions to alloys with 0.5 and 1% Nb. Particularly by comparing the curves for the plain Zr-1% Nb alloy and that with an addition of 0.02% Ca you will notice this effect. The lowest corrosion rate among the Zr-Nb-Ca compositions which now run more than 6000 hours was obtained with the alloy Zr-0.5%Nb-0.5%Ca.

With Cu additions a further improvement of the Zr-Nb alloys was possible. The optimum corrosion resistance was found with contents of 1% Nb and 1% Cu. This alloy

was independently investigated by B.Cox, but he got much higher weight gains, at the same temperature and pressure we used¹⁷⁾. However, B.Cox examined his alloys in the cast-condition which usually is less corrosion resistant than the cold-worked or α -annealed condition. After including annealed samples in his program Cox obtained corrosion rates which are in good agreement with our results on cold-worked samples¹²⁾.

For comparison we included the "ATR" alloy Zr-0.5%Cu-0.5%Mo in our testing program (sheet manufactured by Imperial Chemical Industries Ltd.). This standard alloy for CO₂-cooled reactors is inferior, in steam at 500°C, to the best Zr-Nb-Ca and Zr-Nb-Cu alloys we investigated.

Figure 6 shows the beneficial effect of two other low-valency elements, Y and Ce (the only element of the rare earths with a reasonably low absorption cross-section for thermal neutrons). With these elements too, additions as low as 0.02 weight-% considerably improve the corrosion resistance of Zr-Nb alloys.

The properties of binary Zr-Y and Zr-Ce alloys have been studied by H.H.Klepfer⁴⁾. But again, as with Ca additions, he got very high corrosion rates of the binary alloys. These elements obviously have a detrimental effect in binary Zr alloys but act very beneficially in the combination with some other alloying elements, particularly with Nb.

Nevertheless, also in Zr-Nb base alloys, Y and Ce additions are less effective than those of Cu or Ca. This is demonstrated in figure 7 which compares the best alloys of each of the groups we discussed above.

You see that Cu takes the first place in the order of effectiveness, Ca the second.

It seems attractive, on a trial base, to combine the beneficial effects of these elements in quaternary and more complex alloys. Some preliminary results of such alloys are shown in figure 8.

In our testing program we also included two binary Zr-Cu alloys which have excellent corrosion resistance in high-temperature steam but too low a high-temperature strength for practical application. The corrosion of these alloys was already investigated by W. R. Thomas⁶⁾ and J.N.Wanklyn et al.⁹⁾. We examined additionally a series of ternary Zr-Cu-Ca alloys, but so far only slight improvements were obtained by the Ca additions. However, as we will see, in some other respects the Zr-Cu-Ca alloys are superior to the binary Zr-Cu alloys. The same conclusion can be drawn in comparing ternary Zr-Nb-Cu with quaternary Zr-Nb-Cu-Ca alloys.

Here I should like to stop talking about corrosion rates and to shift to another aspect of the corrosion behavior of Zr alloys in high-temperature steam.

3.2 Oxide layers

The corrosion resistance of Zr alloys can not be characterized exclusively in terms of corrosion rates. The lifetime of Zr alloys in superheated steam is not only determined by the thickness of the oxide layer but also by its quality, more precisely by its tendency towards cracking and spalling. Colour, crack pattern and crack sensitivity of the oxide layers formed

in high-temperature steam differ appreciably with alloy compositions as was outlined elsewhere¹⁸⁾.

We investigated by microscopic means the oxide layers which resulted from two months exposure in steam at 500°C, 1 atm. The metallographic sections of some alloys showed clearly that the cracks do not extend to the bottom of the film, but rather stop at a narrow zone which is darker in appearance and forms the boundary towards the metal (figure 9). This dark band was also observed by J.N.Wanklyn⁹⁾ and referred to as crack-free band. However, contrary to his results, we found the band only on part of the alloys. We have not yet been able to see any systematic relationship between the appearance of the band and the alloy composition. Where the band did appear, it was generally between 10 and 20 μ thick. The width of the band remains constant at the points where cracks occur, although the bulk layer of oxide shows increased thickness due to the faster penetration of oxygen along the cracks.

With a few of the alloys, particularly with Cr-, V- and Cu-bearing alloys, a bright metallic zone of 3 to 5 μ in width was observed along the metal/oxide interface. ^(fig. 10) Microhardness measurements showed that this zone is considerably harder than the alloy matrix. This may be explained in terms of increased oxygen content of the metallic matrix near the metal/oxide interface.

In addition to the cracks passing through the oxide layer perpendicularly, cracks parallel to the surface were also observed in many cases (figure 11). As we pointed out previously¹⁸⁾, it seems very likely from

64 days steam 500°C, 1 atm.

0 ——— 100 μ

0 ——— 20 μ

ZrNr 2,5 Cu 0,5

Ar-melted, 50% cold-worked

§
SIEMENS

Oxide layers of corroded Zr-alloys

Gl
615 831e

64 days steam 500°C, 1 atm.

0 ——— 100 μ

ZrNb1Cr0,5

ZrNb1V0,5

Ar-melted, 50% cold-worked

SIEMENS

Oxide layers of corroded Zr-alloys

Gl
615828e

64 days steam 500°C, 1 atm.

40 μ
|
0

*zircaloy-4 (0,25 Fe)
Ar-melted, 50% cold-worked*

SIEMENS

Oxide layers of corroded Zr-alloys

*Gl
615829 e*

the micrographs that the perpendicular cracks develop prior to the parallel cracks. We assume that the development of parallel cracks out of perpendicular cracks initiates the breakaway of the oxide. Up to this stage the oxide adheres to the metal in spite of severe cracking.

The crack sensitivity of the oxide obviously depends on the alloy composition. But we are still far from knowing the systematic relations between oxide cracking and the individual alloying elements. Much more work should be done on the morphology of oxide layers in dependence of Zr alloy composition.

3.3 Hydrogen embrittlement

After speaking about corrosion rates and oxide layers we should finally mention another phenomenon which, for some Zr alloys, may be considered the worst effect during corrosion: the hydrogen embrittlement.

It is well known that the embrittlement of Zr alloys due to hydrogen pick-up and subsequent hydride precipitation depends essentially on the composition of the alloy¹⁸⁻²¹⁾. I don't want to speak here about the studies we do on the relation between the various types of hydride precipitations and the mechanical properties of Zr alloys. The results of this work being done within a US/Euratom research contract¹⁹⁾ will be published elsewhere. There, it also will be shown that the curve of hydrogen pick-up versus weight gain shows four distinct sections, the three which B.Cox observed²²⁾ and a fourth one which occurs at oxygen weight gains above 100 mg/dm^2 and whose starting point corresponds to the transition point of the alloys.

Here I should only like to present some results on the influence of various alloying elements onto the ductility of Zr alloys corroded in high-temperature steam.

For quick screening we used the bend test. The corrosion coupons of 0.7 mm thickness were bent around a mandrel (3.5 mm diameter). When the first macroscopic crack initiated the slow bending procedure was stopped and the bend angle measured. Since the ductility of hydrided Zr alloys depends very much on the orientation of the sample, as was pointed out elsewhere¹⁸⁾, all alloys were bent in the same manner. The axis of bending was parallel to the rolling direction.

A selection of bend ductility data is presented in figure 12. The graph shows the bend angles after 32 days exposure in steam at 500°C. The pronounced embrittlement of Zry-2, Zry-4 and some other Zr-Sn base alloys becomes obvious from this figure. The binary alloy Zr-1%Nb also shows limited ductility. But ternary additions considerably increase the critical bend angles. Particularly effective is the addition of Fe, whereas Mo is the least effective element we investigated.

Good bend ductilities resulted from Zr-Cu base alloys. Ternary Ca additions were quite beneficial. Outstanding ductility was also shown by quaternary Zr-Nb-Cu-Ca alloys. It is interesting to note that Ca additions seem to have a strong tendency to increase the ductility or, in other words, to counteract hydrogen embrittlement. On the other hand we found that Ca additions simultaneously can increase the hardness of Zr alloys.

For instance, the Vickers Hardness (20 kg load) of the binary alloy Zr-1% Cu can be raised by the additions

FIG. 7-12.

of 0.5% Ca from 215 to 255 in the 50% cold-worked condition, and from 158 to 215 in the annealed condition (15 min 700°C).

From this it appears that Ca additions to Zr alloys may be beneficial from several points of view. A more detailed evaluation about this subject is now in progress.

4. Conclusions

I tried to present you a brief survey of the work which is being done in our laboratory on the development of improved Zirconium alloys for high-temperature steam service. From the results which are available up to now, several conclusions may be drawn:

- a) Zr-Nb alloys with about 0.5 to 2.5% Nb are considerably more corrosion resistant in steam above 400°C than Zircaloy-2 and Zircaloy-4.
- b) The corrosion rates of binary Zr-Nb alloys in the range of 0.5 to 1% Nb can be lowered to a great extent by several ternary alloying elements. Beneficial effects have been stated (at least for certain concentration levels) with the elements Cu, Ca, Y, Ce, V, Cr, Mo, W, Fe, Ni.
- c) Generally it is not possible to estimate the influence of ternary additions on the corrosion resistance from their effectiveness as binary additions.
- d) The effectiveness of a ternary alloying element may very much depend on the concentration level. It is insufficient, therefore, to compare the effectiveness of several ternary alloying elements on the base of

just one concentration level.

- e) The embrittlement of Zr-Nb alloys due to hydrogen pick-up during corrosion in steam is lower than that of Zircaloy-2 and Zircaloy-4. It can very remarkably be influenced by ternary additions. The embrittlement is very largely reduced by small additions of Ca. Also Fe additions are quite beneficial, whereas Mo bearing alloys embrittle rather quickly during steam corrosion at 500°C.
- f) Some of the ternary alloying elements which reduce the hydrogen embrittlement, simultaneously increase the hardness of the alloy. This is particularly true with Ca additions.
- g) It seems not yet possible to establish systematic relationships which could enable us to explain or even to predict the effects which alloying elements have on the corrosion behavior of Zirconium alloys. However, it can be assumed that there are still a great many possibilities of improving the Zirconium alloys employed in our present day reactors.

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ZIRCONIUM ALLOY DESIGN FOR STEAM SERVICE

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Zirconium Alloy Design for Steam Service*

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A program has been initiated under the Joint U.S.-Euratom Research and Development Program 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.⁽¹⁾ The selection of the field of alloy compositions having promise for meeting these specifications has been made.⁽²⁾ Thirty-one alloys whose compositions were chosen from the alloy field have been arc-melted, fabricated to sheet, and heat treated. Over 1800 specimens have been cut from the sheet and put into test for response to composition.⁽³⁾ 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.

The development of nuclear power reactors, and therefore the demands for new zirconium alloys, is still very dynamic. In thermal neutron-spectrum reactors the intrinsic neutron economy of zirconium will force consideration of zirconium-base alloys for new applications. The specific requirements for these various applications will undoubtedly cover a broad spectrum. The best zirconium alloy composition for each of these requirements will vary across an equally broad spectrum. Compositions best suited for sodium-cooled reactor fuel cladding are, for example, not those best suited for water-cooled reactor pressure tubes. The general metallurgical problem to which the Zirconium Alloy Design Program is related is that of the rapid design of a zirconium-base alloy for any of these new nuclear applications. The word "design" is purposely chosen here in place of the word "development." By definition "develop" means "to evolve, to unfold gradually, and to make usable." It is the thesis of this program that with the existing metallurgical

*Work performed under the Joint U.S.-Euratom Research and Development Program under U.S.A.E.C. Contract AT(04-3)-189, Project Agreement 24.

and industrial base of zirconium technology a more direct approach should be pursued. The word "design," which is defined: "to fashion or designate according to a plan or scheme for a specific purpose," comes closer to describing the approach that should be pursued.

The design approach requires first the development of specifications for an acceptable alloy in a specific application in order to define the target for the metallurgical plan. A rigorous scheme for alloy selection to meet these specifications would be the use of mathematical relationships giving nuclear properties, cost, strength, ductility, and corrosion behavior as a function of composition and microstructure. A more realistic plan for the design of zirconium alloys would be the use of (1) a microstructural understanding of the strengthening mechanisms in zirconium supported by empirical data and by phase diagram and transformation kinetics studies for important alloy additions, and (2) the use of a theory of corrosion and hydrogen up-take which includes the dependence on microstructure and alloy composition and is supported by the existing empirical data. It will be clear that even this more realistic plan suffers from deficiencies in the theoretical and empirical understanding of zirconium alloys.

The derivation of specifications and the selection of the alloy field for the Zirconium Alloy Design Program have been reported in detail elsewhere.^(1,2) It is the purpose of this paper to delineate the specific theoretical and empirical deficiencies in the understanding of zirconium alloys which have been found to block the full application of the alloy design approach to the designation of zirconium alloys for steam service. It is proposed that the design approach is justified not only by its success in bringing forth new alloys but also by focusing attention in this way on the most critical problems requiring research emphasis.

SPECIFICATIONS FOR DESIGN OF A ZIRCONIUM ALLOY FOR STEAM SERVICE

Specifications were 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 and resistance to degradation of mechanical properties during service are the primary and critical requirements.⁽¹⁾ 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 0.05% over that for a pure zirconium 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 the 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% or a sheet impact test energy-absorption value of at least 2 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 an initial room temperature ductility defined by the values 20% elongation to failure or 35% reduction in area or better.
6. The alloy shall be as strong as sponge zirconium or stronger.

The specifications for the structure insensitive properties of neutron economy and cost and for the less critical strength and ductility factors could be written in a straightforward way. However, in writing the specifications for susceptibility to hydrogen embrittlement and for long-term corrosion behavior, it was necessary to rely heavily on judgement. Less than precise assumptions had to be employed in the absence of complete empirical and theoretical data. This will be illustrated in the following paragraphs.

a. Corrosion Penetration and Corrosion Product Loss to the System

A corrosion allowance of 10% of the component wall thickness is not unreasonable. Thus a 3-mil corrosion tolerance for a 30-mil fuel cladding wall might be reasonable and thus a tolerable corrosion rate of 1 mil per year

(1.67 mg/dm²/day (mdd)) would be acceptable for a 3-year service life. 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.

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 the 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 400°C and after 1000 hours in steam at 482°C, and we have found no alloy which had a black, tightly-adherent film at weight gains above about 500 mg/dm². 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/dm² is found in the recent work of Pemsler.⁽⁴⁾ He finds the onset of cracking in the films at elevated temperatures (700°C to 750°C) to be at about 500-600 mg/dm². For three-year service life applications, 500 mg/dm² limits the post-transition corrosion rate which is tolerable to 0.5 mdd. For 10 years service this rate would cause spalling at an average rate of no greater than 0.5 mdd over 7 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.⁽⁵⁾ One exception to the observation of some corrosion product loss to the system at 500 mg/dm² which gives some hope of relaxation of this limit was the observation of Douglass⁽⁶⁾ that a zirconium-columbium-chromium alloy had a black adherent film at a weight gain of 3000 mg/dm². 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 there could be a relaxation in the tolerable corrosion rate still further. The maximum tolerable rate of oxide loss to the system is not likely to exceed 5 mdd, however.⁽⁵⁾

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 variously reported. The effect has been reported to be an increase of a factor of 2 by Krenz⁽⁷⁾ and an increase in the rate of corrosion of at least 4.3 according to Nelson and Parker.⁽⁸⁾ 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 across the cladding and perhaps due to the chemical impurities in the coolant or crud.) Cox⁽⁹⁾ also reported early transition and 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 found ourselves in the situation where we would anticipate that the radiation might increase the rate of corrosion in service by anywhere from 1 to 8 times. This meant that the limits which we were deriving 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 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.

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

b. Corrosion Hydrogen Production

The limits of tolerable corrosion rates include those determined by the hydrogen embrittlement which involves a number of factors including 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.

It appeared from all of the data available that in steam the percent of corrosion hydrogen passing through thick, post-transition films would vary greatly with alloy content up to 100%, but probably could not be expected to be below about 10-15% which is the lowest that has been observed in steam (columbium and vanadium binary alloys at 400°C in steam). More realistic expectations for the percentage hydrogen passing through thick corrosion films would be on the order of 25-35%.

No systematic study of the effect of alloying elements on the solubility for hydrogen in zirconium has been reported. However, the solubility is known for hydrogen in Zircaloy-2. Brown and Hardie⁽¹¹⁾ 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 variety of alloying elements. We saw none with the exception of additions of columbium.^(12,13) From these considerations it would appear that the practical upper limit for solubility of hydrogen is still quite low (and is suggested here in Figure 1 which combines the data of Sawatsky⁽¹⁰⁾ and those of Hardie⁽¹⁴⁾ and our metallographic observations.⁽¹³⁾)

The fact that hydride precipitation would give rise to a decrease in ductility of zirconium was first reported by Mudge⁽¹⁵⁾ 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

Figure 8-1. GENERAL FORM OF HYDROGEN SOLUBILITY IN ZIRCONIUM ALLOYS. DATA OF SAWATSKY FOR Zr-2.

Burton.⁽¹⁶⁾ 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.^(17,18) 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.⁽¹³⁾ 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 as well-distributed, thin platelets, within the microstructure.

The exact limits for hydrogen in zirconium alloys in the practical sense have been considered by a number of investigators. The earlier studies⁽¹⁹⁾ 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 subsequently been found to be conservative and later studies, for example those of Canadian⁽²⁰⁾ and British⁽⁹⁾ 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.⁽²¹⁾ indicate that in irradiated Zircaloy-2 (high in nickel) there is no effect of up to 500 ppm hydrogen on ductility. An examination of the phase diagrams 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. 16 and Rösler's tensile data, Ref. 22.) Therefore, for the purposes of this study, 1500 ppm hydrogen in excess of the solubility limit was 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. These various factors of percentage hydrogen pickup, solubility for hydrogen, hydrogen embrittlement, and that of radiation environment are related in Tables I, II, and III as examples.

TABLE I

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

Operating temperature	25	300	400	500	600 °C	
Solubility	8	120	290	600	1070 ppm	
G. B. network (1500 + sol.)	1508	1620	1790	2100	2570 ppm	
Equivalent ΔW_o @ 100% H ₂ pickup for 25-mil tube corroding on one side	360	430	470	550	680 mg/dm ²	
Limit ΔW_o - no radiation for 25-mil wall tube cor- roding on one side 3-year service	0.33	0.39	0.42	0.50	0.62 mg/dm ² /day	
Limit ΔW_o in out-of-pile test to allow for radia- tion increase in post- transition rate of:	2.0x	0.16	0.19	0.21	0.25	0.31 mg/dm ² /day
	4.3x	0.08	0.09	0.10	0.12	0.14 "
(3-yr. service for 25- mil wall <u>corroding on</u> <u>one side</u>)	8.0x	0.04	0.05	0.05	0.06	0.07 "

TABLE II

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

Operating temperature	25	300	400	500	600°C	
Solubility	8	120	290	600	1070 ppm	
G. B. network (1500 + sol.)	1508	1620	1790	2100	2570 ppm	
Equivalent ΔW_o @ 10% H ₂ pickup for 25-mil tube corroding on one side	2600	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	
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 "

TABLE III

MAXIMUM ACCEPTABLE CORROSION RATES ASSUMING MAXIMUM REASONABLESOLUBILITY, 10% H₂ PICKUP AND GRAIN BOUNDARYNETWORK OF HYDRIDE AS LIMITING

Operating temperature	25	300	400	500	600°C
Solubility	480	590	770	1180	1650 ppm
G.B. network	1980	2090	2270	2680	3150 ppm
Equivalent ΔW_o @ 10% H ₂ pickup for 25-mil wall ² corroding on one side	4820	5530	6000	7000	8300 mg/dm ² (Here oxide spalling to system or corro- sion penetration 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
Limit ΔW_o in test out-of- pile to allow for radia- tion increase in post- transition rate of:	2.0x 4.3x	2.2 1.0	2.5 1.2	2.7 1.3	3.2 1.5
3-yr. service for 25-mil wall corroding on one side	8.0x	0.56	0.62	0.69	0.80 0.95

In Table I we have taken the hydrogen solubility data for Zircaloy-2⁽¹⁰⁾ 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 was done, we then considered a specific life; that is, the 25-mil wall zirconium tube corroding from one side (which is equivalent to a 50-mil sheet corroding on both sides) for 3 years. Furthermore, we calculated in the table the tolerable corrosion rates for 3 different possible factors for the effect of radiation for 3-year service. It will be noted in this case the limits for acceptable corrosion 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 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 II we have used the same assumptions except in this case we have assumed the lowest reasonable pickup of the hydrogen, 10%. In this case it appears that with low hydrogen pickup, the metal loss to the system and the penetration by corrosion into the wall will be the limiting case, not hydrogen pickup.

In Table III 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 pickup 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 by hydrogen embrittlement. Assuming the high conceivable solubility limit, we find that the hydrogen embrittlement becomes the limiting factor at hydrogen pickup fractions (for thick films) on the order of 20-25%. 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⁽²³⁾ and some of our data for different alloys are given in Figures 2, 3, and 4. We have therefore purposely used the 100% and 10% (experimentally observed) cases for simplification. Our conclusions in the 10% pickup case will not be changed by the pickup 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.

It is our judgement that an ex-reactor test corrosion specification for the zirconium alloy design for steam service should be 1 mg/dm²/day. It is clear, however, that the acceptable limit may be as high as 5 mg/dm²/day, which is an upper bound set by the limit on corrosion penetration if not by radioactive corrosion product loss to the coolant system. It also must be

Figure 8-2. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

Figure 8-3. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

Figure 8-4. HYDROGEN WEIGHT GAIN AS A FUNCTION OF FILM THICKNESS.

admitted that the acceptable limit may be as low as $0.005 \text{ mg/dm}^2/\text{day}$, which would be set by a radiation service increase of a factor of eight, 100% pickup, hydrogen solubility like that of Zircaloy-2 and a hydride limit of 150 ppm in excess of the solubility limit. (This low hydride limit is conceivable due to unfavorable orientation of hydride platelets and/or local concentration due to thermal gradients.)

The major causes for this lack of precision in the essential first step in zirconium alloy design are neither a lack of knowledge about hydrogen solubility (which one can probably predict within a factor of three for a new alloy) nor a lack of knowledge of percentage hydrogen pickup (which one can probably predict within a factor of two for a new alloy). We found the most critical deficiencies (factors which cannot presently be analytically predicted within a factor of 8 to 10) to be:

- (1) that no complete empirical and theoretical analysis has been made of the effect of hydrogen on the mechanical properties of a variety of zirconium alloys,
- (2) that the effects of neutron radiation, heat transfer, and other special reactor environmental conditions have not been studied in depth for a variety of zirconium alloys, and
- (3) that the limit has not been established for corrosion weight gain prior to corrosion product spalling, nor has the system tolerance for such radioactive corrosion product loss been established.

SELECTION OF ALLOY ADDITIONS

We 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 had been derived. The alloy field 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.⁽²⁾ Alloys in this alloy field were given a 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 was controlled at less than 50 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.

It was found that the selection of alloy additions permissible by the specifications on neutron economy and cost could be based on calculation. The requirements for strength and ductility could be handled in a straightforward manner. Enough empirical data was available to select alloying elements and range of composition which should assure a low percentage hydrogen pickup. It was obvious from the derivation of the specification that the most critical factor in selecting alloying addition was the realization of the lowest possible post-transition corrosion rate at the highest possible temperature. The greatest deficiency in theory was found in just this matter as is illustrated in the following paragraphs.

Referring to Figures 5, 6, and 7, it can be seen that a large number of the alloying elements were 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. This evidence and experience was reviewed in detail.

Examples of alloying elements which lead to good corrosion resistance in steam are iron and chromium which have been studied by Pemsler^(24,25) and by others, and also copper, based on the Canadian work reported by Thomas⁽²⁶⁾ and the work at the Argonne National Laboratory reported by Greenberg.⁽²⁷⁾ 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.⁽²⁸⁾ These four elements were recommended on the basis of their effect on steam corrosion resistance.

The case of silicon additions (and incidently tellurium⁽²⁹⁾ and antimony⁽³⁰⁾ additions) is an interesting one. Additions of silicon to zirconium were first reported to be deleterious in their effect on corrosion resistance.^(31,32) The recent studies of Metallgesellschaft⁽³³⁾ 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.⁽²⁹⁾ 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 were, therefore, not considered of primary interest in the alloy design.

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 8-5. ALLOYING ELEMENTS ELIMINATED FROM THIS ZIRCONIUM ALLOY DESIGN BY NUCLEAR CONSIDERATIONS ALONE

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**

Ce	Pr	Nd		Tb		Ho	Er	Tm	Yb	Lu
----	----	----	--	----	--	----	----	----	----	----

Figure 8-6. ALLOYING ELEMENTS ELIMINATED FROM THIS ZIRCONIUM ALLOY DESIGN BY COST CONSIDERATIONS

Eliminated Due To Deleterious Effects On Corrosion Resistance

Eliminated From Primary Interest On The Basis Of A Combination Of Considerations

Figure 8-7. ALLOYING ELEMENTS ELIMINATED FROM THIS ZIRCONIUM ALLOY DESIGN ON THE BASIS OF CORROSION RESISTANCE

Finally, all but four of the alloying elements (as shown in Figure 7) were eliminated from this study.

The major deficiency in making a precise selection of alloy additions in the alloy design approach was found to be the lack of 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 eliminated 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⁽³⁴⁾ 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 were forced to make the conservative assumption that the effect of the alloying elements which are deleterious by themselves, would be to lead to poor corrosion resistance when in combination with other elements.

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THE DETERMINATION OF THE EQUILIBRIUM
PHASE DIAGRAM, ZIRCONIUM-NIOBIUM

zr-nb
by

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THE DETERMINATION OF THE EQUILIBRIUM
PHASE DIAGRAM, ZIRCONIUM-NIOBIUM

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ABSTRACT

The zirconium-niobium system was systematically investigated to establish the equilibrium phase diagram from 0 to 100 percent of alloy addition. The phase equilibria were determined by metallographic techniques with the auxiliary aid of hardness determinations and incipient-melting techniques.

A minimum in the liquidus-solidus boundaries occurs at 22 weight-percent niobium and 1740C. Complete solid solubility exists above 970C in the body-centered cubic phase. A monotectoid reaction exists at 20 weight-percent niobium and 610C. Solid solubilities at the monotectoid level are 0.6 and 85 weight-percent niobium, respectively.

SUMMARY

The important characteristics of the zirconium-niobium equilibrium phase diagram, as determined by microscopical methods, are listed below.

1. A minimum in the liquidus-solidus boundaries exists at 22 weight percent niobium and 1740C.
2. A continuous solid solution exists in the body-centered cubic phase at and above 970C.
3. The monotectoid reaction occurs at 20 weight-percent niobium and 610C.
4. The maximum solid solubility of niobium in alpha-zirconium is 0.6 weight-percent niobium at the monotectoid level.
5. The solid solubility of zirconium in niobium at the monotectoid level is approximately 85 weight-percent niobium. Below the monotectoid level, the niobium solvus has a steep slope.
6. A Widmanstätten-platelet phase exists in zirconium-rich alloy structures. The phase occurs in only those alloys quenched from beta-containing structures between 8 and about 35 weight-percent niobium. A hardness peak associated with this phase occurs at 9 weight-percent niobium in each series of alloys annealed and quenched from the same temperature level at all levels above the monotectoid.

The research and development efforts expended on zirconium and zirconium alloys in recent years have resulted in the selection of several zirconium-base materials which show good potential for application as nuclear-reactor fuel-cladding. The zirconium-niobium system is one for which much promise is expected. One of the first requirements in developing an alloy for use is the determination of its equilibrium phase diagram. It was this reason that prompted the present study.

Up until the time this research was initiated, there had not been a thorough metallographic investigation of the phase equilibria of the zirconium-niobium system, and the limited partial studies that existed demonstrated much conflict in the values of the compositions and temperatures of the important features.

The only previous determination of the entire diagram was conducted by Rogers and Atkins (1) who used resistivity, dilatometric, X-ray diffraction, and incipient-melting techniques. Rogers and Atkins found a minimum in the liquidus-solidus boundaries at approximately 22 weight-percent niobium and 1740C, and they reported complete solid solubility in the body-centered-cubic phase above 1000C. A monotectoid reaction was located at 17.5 weight-percent niobium and 610C. The solid solubilities at the monotectoid level were 6.5 and 87 weight-percent niobium, respectively. Domagala and McPherson (2) conducted a limited metallographic survey in the zirconium-rich region and reported a monotectoid reaction at 17 weight-percent niobium and 800C, the existence of continuous solid-solubility above 1180C, and the maximum solid-solubility of niobium in alpha-zirconium to be less than 5 weight-percent niobium. Bychkov, Rozanov, and Skorov (3) used incipient melting, dilatometry, thermal analysis, X-ray diffraction, and metallography in a cursory study. They reported the liquidus-solidus

minimum at 25-28 weight-percent niobium and 1600C. The monotectoid reaction was determined to occur at 12 weight-percent niobium and 560C. Dwight (4) used X-ray diffraction and metallographic techniques and reported the monotectoid reaction at 13.5 weight-percent niobium and 590C.

EXPERIMENTAL PROCEDURE

Alloys were prepared from high-purity, low-hafnium, iodide-process zirconium and Grade I, electron-beam-melted niobium. The zirconium was obtained in crystal-bar form from the Pittsburgh Naval Reactor Group, and the niobium was obtained in ingot form from the Wah Chang Corporation. Table I lists typical analyses for the pure metals.

Typical Analyses of Zirconium and Niobium Metals

<u>Iodide-Process Zirconium</u>		<u>Electron-Beam-Melted Niobium</u>	
Al	0.01%	Al	< 20 ppm
Be	0.0001	B	< 1
C	0.005	C	< 30
Cr	0.01	Nb	> 99.8%
Fe	0.01	Cd	< 1 ppm
Hf	0.01	Co	< 20
Mg	0.005	Cr	< 20
Mn	0.01	Cu	< 40
N	0.001	Fe	< 100
Ni	0.007	Mg	< 20
O	0.010	Mn	< 20
Pb	0.005	Mo	< 20
Sn	0.005	N	40
V	0.005	Ni	< 20
		O	50
		Pb	< 20
		Si	< 100
		Sn	< 20
		Ta	620
		Ti	< 150
		V	< 20
		W	< 300
		Zn	< 20
		Zr	< 500

The alloys were melted in a water-cooled, copper-hearth arc furnace using a tungsten-tipped electrode and an argon atmosphere. Nominal

alloy compositions were determined by noting the weight losses after arc melting. These weight losses were negligible, being on the order of about 0.03 weight-percent.

Alloys were melted to provide enough different compositions to study the system from 0 to 100 weight-percent of alloy addition. Alloy compositions ranged by one weight-percent increments from pure zirconium to pure niobium. In addition, 0.2, 0.4, 0.6, and 0.8 weight-percent niobium alloys were melted to determine the zirconium solvus boundary.

Before isothermal-annealing heat-treatments were initiated, it was necessary to perform certain pretreatments on the alloy button-ingots. The pretreatments consisted of cold pressing, homogenizing for eight hours at 1400C in a high-temperature vacuum-furnace, and cold rolling. The pretreatments were conducted to attain equilibrium more quickly in the subsequent isothermal-annealing heat-treatments.

The alloys for isothermal annealing were sealed in quartz or Vycor capsules under a partial pressure of argon, and the capsules were annealed in either resistance-wound or Globar, vertical-tube furnaces. The temperature control was $\pm 2^{\circ}\text{C}$ of the desired temperature. The alloys were rapidly quenched by dropping and crushing the capsules in cold water. Diffusion in the solid state in niobium-rich alloys occurs very slowly even at high temperatures. For this reason, some of the isothermal-annealing heat treatments were extended as long as six months in duration.

The etching characteristics of the annealed-and-quenched alloys varied widely, and much care was necessary to produce the true micro-structures. The polishing operation was a critical step, and the following technique was used: after grinding on 80, 120, 400, and 600-grit

abrasive papers, the specimen was briefly polished on a wheel with 6-micron diamond paste; the specimen was then transferred to a Syntron vibratory polisher for two stages of polishing with 5-micron and 0.3-micron alumina. Etching was accomplished with water-base etchants containing varying amounts of HF, HNO₃, and H₂O₂. Another etchant for zirconium-rich alloys employed NH₄F as an addition to the water-base etchant. The proportions depended upon the compositions and annealing temperatures of the specimens. It was found that H₂O₂ is a desirable reagent in the etchant to etch those specimens in the beta-zirconium plus beta-niobium field and the beta-niobium plus alpha-zirconium field. In these two-phase regions, the second phase occurs as a very fine precipitate. It is believed that the H₂O₂ inhibits the action of the etchant on the precipitate and allows the etchant to attack the matrix. However, it was still difficult to interpret the low-temperature, niobium-rich specimens because the precipitate was so fine.

The majority of the data for the determination of the liquidus-solidus boundaries was obtained by incipient-melting techniques. The fusion-point technique was used as an auxiliary aid. Incipient melting was performed on a notched specimen suspended in an evacuated molybdenum-tube, resistance furnace. The technique consists of heating the specimen until the first signs of melting occur in the notch while observing this temperature with a Leeds and Northrup optical pyrometer. The congruent-melting point of the minimum in the liquidus-solidus was determined in this manner. The solidus and liquidus temperatures of other alloys throughout the diagram were determined by a combination of incipient-melting and fusion-point techniques. The fusion-point furnace consists of an enclosed chamber with a V-shaped

tungsten-strip element fastened between two water-cooled copper electrodes. The specimen was placed in the V-shaped portion of the tungsten element--only point contact between the specimen and the element occurred. A purified helium atmosphere was used in the chamber. The specimen was rapidly brought to its melting point by electrical-resistance heating of the tungsten-strip element. By careful observation with an optical pyrometer, both the solidus and liquidus temperatures were obtained with this apparatus.

The incipient-melting and fusion-point apparatuses were temperature calibrated prior to determination of liquidus-solidus temperatures in the zirconium-niobium system. A standard curve was constructed for each apparatus by observing the melting points of pure metals with well-established melting points such as copper, nickel, platinum, and rhodium.

RESULTS AND DISCUSSION

A graphical representation of the phase equilibria of the zirconium-niobium system is presented in Figure 1. The diagram is based primarily on the interpretation of microstructures of isothermally-annealed and quenched alloys. The characteristic temperatures and compositions are designated on the diagram; however, the experimental points have been omitted for the sake of clarity.

The principal features of the complete diagram may be summarized as follows:

1. A minimum point exists in the liquidus-solidus boundaries at 22 weight-percent niobium and 1740C.
2. Complete solid solubility occurs throughout the diagram above 970C in the body-centered cubic phase (beta).

FIGURE 9-1 Equilibrium Phase Diagram of the Zirconium-Niobium Alloy System

3. The allotropic-transformation temperature from beta-to alpha-zirconium is lowered by the alloy addition of niobium to 610C at 20 weight percent niobium where a monotectoid reaction occurs:

4. The monotectoid loop extends from 20 to about 85 weight-percent niobium and reaches a maximum at about 60 weight-percent niobium and 970C.
5. The maximum solid solubility of niobium in alpha-zirconium at the monotectoid level is 0.6 weight-percent niobium.
6. The solid solubility of zirconium in niobium at the monotectoid level is approximately 85 weight-percent niobium.
7. A Widmanstatten-platelet phase occurs abruptly at 8 weight-percent niobium in beta-quenched alloys and exists similarly in compositions up to about 35 weight-percent niobium. In alloys with less than 8 weight-percent niobium, the beta-zirconium quenches to acicular alpha-zirconium. A hardness peak occurs at 9 weight-percent niobium. Alloys in this composition range that are isothermally annealed below the monotectoid level do not exhibit the peak. This indicates that the platelet phase is a transition phase formed from the beta-zirconium solid solution.

The phase equilibria in the zirconium-rich region of the zirconium-niobium diagram are presented in Figure 2. Many of the experimental points were left out because space would not permit their inclusion. The diagram extends graphically from 0 to 50 weight-percent niobium. The niobium-rich portion is described later in the paper.

FIGURE 9-2 Zirconium-Rich Portion of the Zirconium-Niobium Equilibrium Phase Diagram

Pure zirconium, on heating, undergoes an allotropic phase transformation for a hexagonal-close-packed (alpha) to a body-centered-cubic (beta) structure at 862 ± 50 (5). However, iodide-process zirconium contains small amounts of impurity elements which cause the transformation to occur over a range of temperature. In a preliminary study, the range of co-existence of alpha and beta was determined with the zirconium charge material obtained for this program. Specimens were prepared with the same pretreatments as described in the previous section. Also, the isothermal annealing and quenching of these specimens were the same as described before. The microstructural data produced from this study revealed that the transformation range was from 830 to 890C for this specific lot of iodide zirconium. Investigations of the phase equilibria in the zirconium-rich region indicated that these impurities were negligible in effecting the position of phase boundaries in the binary system. Therefore, the transformation temperature of 862C is used in the construction of the phase diagram.

The phase equilibria of the zirconium-rich region is characterized by an additional structural phenomenon which does not show in the diagram in Figure 2. The existence of a Widmanstatten-platelet phase between 8 and about 35 weight-percent niobium in all alloys cooled from the beta-zirconium phase is revealed in their respective microstructures. The platelet phase is thought to be a metastable transitional phase formed at the monotectoid temperature. Since the phase diagram of Figure 2 is an equilibrium phase diagram, the platelet phase and its range of existence are not represented by phase boundaries. Furthermore, the presence of the platelet phase did not interfere with the interpretation of the equilibrium phase boundaries, but it did result in some

interesting microstructures. The existence of a transition phase which has been termed "omega" is well known in other zirconium and titanium systems (6,7,8,9). The Widmanstätten structure and an "omega" phase associated with it in the zirconium-niobium system have been the object of a kinetics of transformation study(6). The conditions under which "omega" nucleates and grows are rather well defined in the reported work.

The scope of this phase-diagram study did not include non-equilibrium studies. Therefore, a detailed study of the characteristics of the formation and existence of the transition phase were not included in the investigation. However, certain observations are included as a by-product of the equilibrium study which illumine the nature of this transition phase.

The delineation of the phase boundaries of the diagram in Figure 2 was accomplished as a result of interpretation of isothermally-annealed microstructures. A representative group of microstructures has been selected and are now presented as typical evidence of the placement of boundaries.

Although the Widmanstätten-platelet phase is not indicated on the equilibrium phase diagram, several photomicrographs are presented to illustrate the mode of precipitation of this transition phase. This phase occurs in all beta-quenched alloys from 8 to 35 weight-percent niobium. The abrupt appearance of the Widmanstätten-platelet phase is illustrated in microstructures of 7 and 8 weight-percent niobium alloys annealed at 850 and 700C. Figure 3 shows a 7 weight-percent niobium alloy which was annealed at 850C. The microstructure of this alloy, which was quenched from an all beta-zirconium field, is that of transformed beta-zirconium. The microstructure in Figure 4 of an 8 weight-

FIGURE 9-3

125x

7 w/o Nb, annealed at 850C
quenched from all β -Zr field.
Transformed β -Zr.

FIGURE 9-4

250x

8 w/o Nb, annealed at 850C,
quenched from all β -Zr field.
Coarse Widmanstätten platelet
phase in a retained β -Zr matrix.

FIGURE 9-5

250x

7 w/o Nb, annealed at 700C,
quenched from α -Zr + β -Zr field.
 α -Zr randomly dispersed in a
transformed β -Zr matrix.

FIGURE 9-6

250x

8 w/o Nb, annealed at 700C,
quenched from α -Zr + β -Zr field.
 α -Zr has precipitated at former
Widmanstätten platelet phase sites
in a retained β -Zr matrix.

percent niobium alloy annealed at this same temperature, 850C, reveals the precipitation of the Widmanstatten-platelet phase in a retained beta-zirconium matrix. Figures 5 and 6 illustrate the effect of the Widmanstatten-platelet phase upon the precipitation of isothermal alpha-zirconium in the alpha-zirconium plus beta-zirconium. The 7 weight-percent niobium alloy (Figure 5) which was annealed at 700C shows alpha-zirconium randomly precipitated in a transformed beta-zirconium matrix. However, the 8 weight-percent niobium alloy (Figure 6), which was also annealed at 700C, reveals that the alpha-zirconium has grown at former Widmanstatten-platelet phase sites. The platelet phase had formed by an earlier homogenization anneal and quench from the beta-zirconium region. Upon reheating to the two-phase region, alpha-plus beta-zirconium, the alpha-zirconium grew at the former sites of the platelet phase. A hardness peak associated with the transition phase occurs at 9 weight-percent niobium in alloys which were quenched from above the monotectoid level in this composition range. The peak was maximum when the alloy was quenched from the all beta-zirconium field compared to those quenched from the alpha-zirconium plus beta-zirconium region.

The maximum solid solubility of niobium in zirconium was found to be 0.6 weight-percent niobium at the monotectoid level of 610C. Alloys of 0.2, 0.4, 0.6, and 0.8 weight-percent niobium were isothermally annealed at 800, 700, 640, 615, and 550C to locate the zirconium solvus. Figures 7 and 8 are photomicrographs of 0.4 and 0.8 weight-percent niobium alloys annealed at 640C which bracket the limit of maximum solid solubility. The microstructure of the 0.4 weight-

percent niobium alloy is single-phase alpha-zirconium while the microstructure of the 0.8 weight-percent niobium alloy is two-phase alpha-zirconium plus transformed beta-zirconium.

The extent of the two-phase field, alpha-zirconium plus beta-zirconium, is shown at both 800 and 640C temperature levels. Figure 9, 10, and 11 are the structures of 0.4, 3 and 5 weight-percent niobium alloys annealed at 800C. The 0.4 weight-percent niobium alloy (Figure 9) shows equiaxed alpha-zirconium with minor amounts of transformed beta-zirconium at the grain boundaries. The 3 weight-percent niobium alloy (Figure 10) is approximately 50 percent alpha-zirconium and 50 percent transformed beta-zirconium. The 5 weight-percent niobium alloy (Figure 11) shows alpha-zirconium precipitated in a transformed beta-zirconium matrix which is representative of a structure approaching the single-phase beta-zirconium region.

Figures 8, 12, 13, and 14 show the extent of the two-phase field at 640C. Figure 8, a 0.8 weight-percent niobium alloys was described earlier. Figures 12, 13, and 14 are structures of 10, 14, and 18 weight-percent niobium alloys that show an increasing ratio of beta-zirconium to alpha-zirconium. Note that the alpha-zirconium has nucleated and grown at former Widmanstatten-platelet phase sites.

The monotectoid level has been established at 610C using both microstructural and hardness data. Figures 15 and 16 are photomicrographs of 3 weight-percent niobium alloys annealed at 620 and 600C, respectively. The alloy annealed at 620C shows alpha-zirconium and transformed beta-zirconium at the grain boundaries. The 600C alloy shows fine-grained transformation products as a result of the

FIGURE 9-7

250x

0.4 w/o Nb, annealed at 640C.
Single-phase α -Zr.

FIGURE 9-8

500x

0.8 w/o Nb, annealed at 640C.
Equiaxed α -Zr and transformed
 β -Zr at grain boundaries.

FIGURE 9-9

250x

0.4 w/o Nb, annealed at 800C.
 α -Zr with transformed β -Zr at
grain boundaries.

FIGURE 9-10

250x

3 w/o Nb, annealed at 800C. 50
per cent α -Zr and 50 percent trans-
formed β -Zr.

FIGURE 9-11

250x

5 w/o Nb, annealed at 800C.
 α -Zr in a transformed β -Zr matrix.

FIGURE 9-12

250x

10 w/o Nb, annealed at 640C. α -Zr
 in a retained β -Zr matrix. α -Zr has
 nucleated and grown at former Wid-
 manstätten sites.

FIGURE 9-13

250x

14 w/o Nb, annealed at 640C.
 α -Zr in a retained β -Zr matrix.

FIGURE 9-14

250x

18 w/o Nb, annealed at 640C. α -Zr
 in a retained β -Zr matrix.

FIGURE 9-15

500x

3 w/o Nb, annealed at 620C. α -Zr plus transformed β -Zr. Quenched from just above the monotectoid level.

FIGURE 9-16

500x

3 w/o Nb, annealed at 600C. α -Zr plus β -Nb. Quenched from just below the monotectoid level.

FIGURE 9-17

250x

20 w/o Nb, annealed at 620C. Retained β -Zr and Widmanstätten platelet phase quenched from just above the monotectoid level.

FIGURE 9-18

250x

20 w/o Nb, annealed at 600C. α -Zr plus β -Nb. Quenched from just below the monotectoid level.

monotectoid reaction. Figures 17 and 18 are photomicrographs of 20 weight-percent niobium alloys annealed at 620 and 600 C. The structure of the alloy annealed at 620C is retained beta-zirconium plus transition phase while the alloy annealed at 600C exhibits the monotectoid transformation products.

Hardness data bracket the monotectoid level in the following manner. Alloys of 8 to 35 weight-percent niobium form a transition phase upon quenching from the beta-zirconium field. The hardness of these quenched alloys attains a maximum at 9 weight-percent niobium. Alloys quenched from 620C and above exhibit this hardness peak, whereas alloys quenched from 610C and below do not. Thus, the monotectoid level is revealed by the respective presence and absence of the characteristic hardness peak at these two temperature levels. This phenomenon is illustrated in Figure 19, which is a plot of hardness versus temperature for four typical annealing temperatures -- 900, 700, 640, and 600C. The relative heights of the hardness peaks as a function of annealing temperature can be explained by the amount of alpha-zirconium present at the annealing temperature.

The monotectoid point has been located at about 20 weight-percent niobium as the next series of photomicrographs of alloys annealed at 640C illustrate. Figure 14, described earlier, presents the structure of an 18 weight-percent niobium alloy which is near the single-phase beta-zirconium region. Figure 20, a 20 weight-percent niobium alloy microstructure, exhibits single-phase retained beta-zirconium plus the transition Widmanstätten-platelet phase. Figure 21 shows a 22 weight percent niobium alloy microstructure. Beta-niobium has

FIGURE 9-19 Hardness of Annealed Zirconium-Niobium Alloys

FIGURE 9-20

200x

20 w/o Nb, annealed at 640C. Single-phase β -Zr and metastable Widmanstatten platelet phase.

FIGURE 9-21

250x

22 w/o Nb, annealed at 640C. β -Nb precipitated at retained β -Zr grain boundaries. Transitory Widmanstatten structure can be seen.

FIGURE 9-22

250x

35 w/o Nb, annealed at 850C. Retained β -Zr and impurity inclusions.

FIGURE 9-23

250x

45 w/o Nb, annealed at 850C. β -Nb precipitated in a retained β -Zr matrix.

precipitated at the retained beta-zirconium grain boundaries.

The delineation of the beta-zirconium and beta-zirconium plus beta-niobium boundary is illustrated in the following figures. Figures 22 and 23 represent 35 and 45 weight-percent niobium alloys annealed at 850C, and Figures 24 and 25 represent 40 and 50 weight-percent niobium alloys annealed at 900C. The former figure, in each case, shows a single-phase, retained beta-zirconium microstructure while the latter, in each group, shows a two-phase microstructure, retained beta-zirconium plus beta-niobium.

A continuous series of solid solutions exist at 970C and above. A series of alloys annealed at 960C and 980C demonstrated that the top of the monotectoid loop is at about 60 weight-percent niobium and 970C. Figures 26 and 27 are microstructures of 60 weight-percent niobium alloys annealed at 980 and 960C, respectively. The alloy annealed at 980C (Figure 26) shows single-phase beta solid solution, and the alloy annealed at 960C (Figure 27) shows the retained beta-zirconium plus beta-niobium structure.

The phase equilibria in the niobium-rich region of the zirconium-niobium diagram are presented in Figure 28. Only those experimental points which could be clearly interpreted are presented; other experimental points were omitted to avoid crowding. The niobium-rich region extends graphically in Figure 28 from 35 to 100 weight-percent niobium.

The interpretation of alloys in this region of the diagram was complicated by several factors. First, the presence of coring after the rigorous pretreatments (cold pressing, homogenization anneal at 1400C for 1 hour, and cold rolling) and the subsequent isothermal

annealing heat treatments was still evident in many of the alloy structures. Since the diffusion rate in niobium-rich alloys is extremely slow, annealing times as long as six months were not sufficient in many cases to completely destroy remnants of coring. The longer homogenization pretreatment (1400C for 8 hours) successfully removed coring, but the number of alloys thus treated was rather limited. Secondly, the niobium-rich alloys are characterized in structure by the presence of amounts of an impurity phase. This phase is attributed to be zirconium oxide. The phase precipitates at grain boundaries, subgrain boundaries, twin boundaries and dislocation sites. The formation of zirconium oxide is thought to be due to the scavenging effect of zirconium on the impurity oxygen content in the as-cast alloy. A specimen was examined for the presence of zirconium oxide by X-ray diffraction techniques; however, the quantity of the phase was so small that the diffraction pattern of this impurity phase could not be detected. Stewart, Lieberman, and Rowe (10) investigated the properties of dilute alloys of zirconium in niobium and noted the presence of the same impurity phase. Positive identification of zirconium oxide was established. Finally, the precipitation of equilibrium second-phase in these alloys occurred in a very fine form, especially below the monotectoid level. As a result of these three factors, the onset of precipitation as the compositions of alloys shift into the two-phase region was difficult to establish accurately. However, the interpretation and placement of the solid solubility at 15 weight-percent zirconium in niobium at the monotectoid level is thought to be accurate within several percent. Below the monotectoid level, the slope of the

FIGURE 9-24

250x

40 w/o Nb, annealed at 900C.
Retained β -Zr plus impurity
inclusions

FIGURE 9-25

250x

50 w/o Nb, annealed at 900C.
 β -Nb at retained β -Zr grain
boundaries.

FIGURE 9-26

250x

60 w/o Nb, annealed at 980 C.
 β quenched from just above the
monotectoid loop. Fine precipi-
tate of ZrO_2 is present.

FIGURE 9-27

250x

60 w/o Nb, annealed at 960C.
Retained β -Zr plus β -Nb quenched
just within the monotectoid loop.

FIGURE 9-28 Niobium-Rich Portion of the Zirconium-Niobium Equilibrium Phase Diagram

solvus boundary appears to be rather steep.

The extent of solid solubility of zirconium in niobium is illustrated in Figures 29 and 30. Figure 29 is the microstructure of an 86 weight-percent niobium alloy annealed at 500C which shows single-phase, beta-niobium. A minor amount of zirconium oxide is present. Figure 20 shows the structure of an 85 weight-percent niobium alloy annealed at 500C. The presence of the fine precipitate appearing at grain boundaries indicates location just within the two-phase region, alpha-zirconium plus beta-niobium. The boundary between beta-niobium/beta-niobium plus beta-zirconium is bracketed by the alloys whose structures appear in Figures 31 and 32. Figure 31 is the structure of a 75 weight-percent niobium alloy annealed at 900C. Single-phase beta-niobium exists with zirconium oxide appearing at twin boundaries. Figure 32 is the structure of a 70 weight-percent niobium alloy annealed at 900C. The appearance of second phase at the grain boundaries indicates this composition is within the two phase region, beta-niobium plus beta-zirconium. Again, minor amounts of zirconium oxide are seen, primarily at twin boundaries.

The solidus-liquidus boundaries were determined throughout the zirconium-niobium alloy system. A minimum in the solidus-liquidus boundaries was established at 22 weight-percent niobium and 1740C. Congruent melting occurs at this composition and temperature. Alloys near this composition were characterized by a narrow temperature range of melting. The boundaries are presented with the complete diagram in Figure 1. The data used to construct these boundaries are presented in tabular form in Table IV.

FIGURE 9-29

500x

86 w/o Nb, annealed at 500C.
 β -Nb with fine ZrO_2 .

FIGURE 9-30

250x

85 w/o Nb, annealed at 500C.
 β -Nb matrix and fine α -Zr pre-
 cipitated at grain boundaries.

FIGURE 9-31

250x

75 w/o Nb, annealed at 900C.
 Single-phase β -Nb. ZrO_2 can
 be seen at twin and grain boun-
 daries.

FIGURE 9-32

250x

70 w/o Nb, annealed at 900C.
 Two-phase. Small quantities of
 retained β -Zr can be seen at
 β -Nb grain boundaries.

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TRANSFORMATIONS IN ZIRCONIUM-NIOBIUM ALLOYS

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TRANSFORMATIONS IN ZIRCONIUM-NIOBIUM ALLOYS

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ABSTRACT

Time-Temperature-Transformation diagrams are presented for the isothermal decomposition of beta in zirconium alloys containing 12%, 17.5% and 25% niobium. Transformation occurs by fundamentally different mechanisms at high and low reaction temperatures. A cellular reaction, analogous to the discontinuous precipitation in many age hardening systems, was observed in the hypermonotectoid 25%Nb alloy but could not be detected in the 12% or 17.5%Nb alloy. The direct precipitation of alpha from beta dominates the high temperature decomposition of the latter alloys. This direct precipitation of alpha also occurs in the 25% alloy at temperatures in the range 475 to 575°C. Here, it competes with the cellular mechanism.

Decomposition of beta at temperatures below 450°C involves the formation of the omega phase characteristic of many beta stabilized titanium and zirconium alloys. This phase can form in either a diffusionless or a diffusion controlled manner. The temperature for initiation

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of the diffusionless transformation during cooling has been determined and found to decrease with increasing niobium content of the alloy. This diffusionless formation of omega appears to take place reversibly and is intimately associated with a negative temperature coefficient of electrical resistivity observed in this and certain other titanium and zirconium alloys. The diffusion controlled, isothermal formation of omega results in a metastable equilibrium involving an enriched beta phase. The ω - β transus line has been identified for this metastable equilibrium.

INTRODUCTION

The subcritical transformations that occur in beta stabilized titanium and zirconium alloys are extremely varied and encompass virtually all of the generally recognized transformation mechanisms. (1-10). Both diffusionless and diffusion controlled reactions are encountered and several distinct mechanisms are involved in each category. This paper describes the results of an experimental study of these transformations in zirconium alloys containing 5% to 25% niobium.

MATERIALS AND PROCEDURE

The principal efforts in this study were concentrated on alloys containing 5%, 12%, 17.5% and 25% niobium.* These alloys were prepared by a double arc melting practice and the cast ingots were encased in stainless steel cans for hot working to 1/8" thick sheet. Charged weights were employed for the niobium contents and contamination of the finished sheets by interstitial elements was, in general, quite low as illustrated in Table I.

*A few tests also were conducted on 7.5% and 10% niobium alloys kindly supplied by Dr. M. L. Picklesimer, Oak Ridge National Laboratory.

TABLE I

Interstitial Content of Alloys

Alloy	%C	%O	%N	%H
5%Nb	.0143	.031	.005	.0017
12%Nb	.0074	.022	.010	.0019
17.5%Nb	.0087	.023	.012	.0018
25%Nb	.0166	.029	.013	.0019

Dilatometric, electrical resistance, x-ray diffraction, metallographic and hardness techniques have been employed to study the transformations. Betatizing was conducted for one hour at 900°C with samples wrapped in zirconium foil and encapsulated in evacuated or helium filled quartz vials. For the quench-aging studies, samples were quenched from the betatizing treatment by breaking the vial in iced brine. Aging and isothermal transformation was conducted in molten salt at temperatures in the range 200 to 640°C. Samples were exposed directly to the salt at temperatures below 550°C and were contained in helium filled capsules for the higher transformation temperatures.

RESULTS AND DISCUSSIONSTRUCTURE OF QUENCHED ALLOYS

The zirconium-niobium equilibrium diagram is characterized by complete solid solubility of niobium and zirconium at high temperatures

and a monotectoid reaction at lower temperatures (1-4). While there is some disagreement among the various investigators concerning the monotectoid temperature and composition, the diagram of Rogers and Atkins, reproduced as Fig. 1 has been used in the present study and correlates well with the results of this investigation.

Two types of structures were observed metallographically in alloys quenched from 900°C. The 5%Nb alloy transformed martensitically to the CPH alpha phase. While alpha was absent from alloys containing 7.5% or more niobium, the beta phase could not be quenched to room temperature without change. Metallographic examination (Fig. 2) revealed small amounts of a second phase distributed in a widmanstatten pattern. This phase has been identified previously (5, 7) and possesses a body centered tetragonal structure in binary zirconium-niobium alloys. Since this phase appears to form and revert at very low temperatures (5), it does not influence the transformations that occur at higher temperatures and, consequently, will not be considered further.

In addition to the BCT phase, the omega phase, which occurs in most beta stabilized titanium or zirconium alloys (7-11), is present after quenching. While omega cannot be revealed metallographically pronounced changes in physical and mechanical properties and in x-ray diffraction patterns are associated with its formation.

FIG. 10-1.: PARTIAL ZIRCONIUM-NIOBIUM EQUILIBRIUM DIAGRAM FROM ROGERS AND ATKINS (1).

(800 X)

FIG. 10-2.: Zr-12% Nb ALLOY

900° C, 1 HR, BRINE QUENCH

CHEMICAL POLISH:

25 ML	HNO ₃
10 ML	HCL
18 ML	HF
25 ML	H ₂ O

The hardness of quenched alloys is presented as a function of composition in Fig. 3. The low hardness of the 5%Nb alloy is characteristic of martensitic alpha while the high hardness of the 7.5% Nb alloy reflects the large amount of omega that forms at this composition. As in other titanium and zirconium systems, the amount of omega in the quenched state decreases with increasing alloy content which is reflected in reduced hardness as well as in the intensity of x-ray reflections. Typical precession patterns of the 12% and 17.5% niobium alloys are presented in Figs. 4 and 5. While the omega reflections are strong and reasonably sharp in the 12% alloy, they are extremely weak and diffuse at the 17.5%Nb level. Omega was essentially absent from the quenched 25% niobium alloy.

TTT DIAGRAMS

The subcritical decomposition of beta has been studied by the aging of samples previously quenched to room temperature and by direct isothermal transformation techniques. The method of heat treatment was found to be without influence on the transformation mechanisms and to influence transformation kinetics only under very special conditions observed in the 12%Nb alloy. Thus, isothermal transformations will be given primary consideration.

The dimensional changes that accompany transformation have

FIG. 10-3. HARDNESS OF QUENCHED ALLOYS

Zr-12% Nb
 900°C, 1HR → ICED BRINE QUENCH
 (hhl) BETA RECIPROCAL LATTICE PLANE
 Mo RADIATION - Zr FILTER

FIG. 10-4. PRECESSION PATTERN 12% Nb ALLOY QUENCHED.

Zr-17.5 % Nb
 900°C, 1 HR → ICED BRINE QUENCH
 (hh1) BETA RECIPROCAL LATTICE PLANE
 Mo RADIATION - Zr FILTER

FIG. 10-5. PRECESSION PATTERN 17.5 Nb ALLOY QUENCHED.

been found quite useful for a qualitative exploration of decomposition kinetics. Typical dilation curves for aging of the 12%Nb alloy are illustrated in Fig. 6. A pronounced expansion accompanies transformation at the higher temperatures and metallographic and x-ray studies reveal that this results from the precipitation of alpha zirconium. The contraction observed at lower temperatures is associated with the formation and aging of omega and will be considered in greater detail shortly.

The influence of reaction temperature and alloy composition on the kinetics of beta decomposition can be summarized most succinctly in TTT diagrams. Such diagrams, constructed from the combined results of dilatometric, hardness, metallographic and x-ray studies, are presented in Figs. 7 to 9 for isothermal transformation of the 12%, 17.5% and 25% niobium alloys. At high temperatures, decomposition is accomplished by precipitation of the equilibrium phases, alpha and β_{Nb} while decomposition at lower temperatures involves formation of the metastable phase, omega. This phase can form in a diffusionless manner during quenching and the temperature for its initiation has been designated ω_s on Figs. 7 and 8. For the 25%Nb alloy, ω_s is at or slightly below room temperature. As demonstrated in the TTT diagrams, omega also can form in a diffusion controlled manner at temperatures above ω_s . Increasing alloy content

FIG. 10-6. DILATION CURVES FOR THE AGING OF THE 12% Nb ALLOY.

FIG. 10-7. TTT DIAGRAM FOR ISOTHERMAL AGING OF THE 12% Nb ALLOY.

FIG. 10-8. TTT DIAGRAM FOR ISOTHERMAL AGING OF THE 17.5% Nb ALLOY.

FIG. 10-9. TTT DIAGRAM FOR ISOTHERMAL AGING OF THE 25% Nb ALLOY.

retards significantly the rates of both the omega and the high temperature reactions.

THE OMEGA REACTION

Single crystal and Debye-Scherrer diffraction techniques were employed to examine the structure of omega in quenched and in isothermally transformed or aged alloys. The diffraction patterns for both conditions agree well with the hexagonal structure proposed for omega in titanium alloys (8, 10). However, significant parameter differences, reflecting major composition differences, exist between the two states. In the aged condition omega in these zirconium alloys has an axial ratio of 0.622; whereas, that formed on quenching has an axial ratio of 0.616.*

The influence of alloy content on the parameters of omega in the quenched and aged conditions is illustrated in Fig. 10. The strict lattice relationship (8, 10) between beta and omega requires that $[11\bar{2}0]_{\omega} // [10\bar{1}]_{\beta}$ and $[0001]_{\omega} // [111]_{\beta}$. The interatomic distances in the $[11\bar{2}0]_{\omega}$ and $[111]_{\beta}$ directions were calculated from the parameters reported by Rogers and Atkins and are included in Fig. 10. Only slight readjustments in interatomic spacing are associated with the formation

*The diffuse reflections from quenched omega in alloys containing 17.5% or more niobium prevent the precise determination of lattice parameters. Single crystal patterns suggest that quenched omega in these higher niobium alloys may not possess this axial ratio of 0.616.

FIG. 10-10. OMEGA PARAMETERS.

of omega during quenching. Thus, it appears that the parameters and axial ratio of omega in the quenched condition are enforced by coherency with the surrounding matrix.*

Metastable Equilibrium of Beta and Omega

In the aged condition, omega attains a metastable equilibrium with a niobium enriched beta phase. This is revealed most clearly in Fig. 10 by the fact that the axial ratio and individual c_o and a_o parameters of aged omega are independent of alloy content. Thus, omega attains a fixed composition - near 6%Nb - in the fully aged condition. The partition of niobium to the surrounding beta that is required to establish this equilibrium has been reported by many investigators (5-11) and is observed experimentally as a streaking and eventual displacement of beta diffraction lines in the direction of increased alloy content.

The lattice parameter of the enriched beta has been used to determine its composition. At constant temperature, the enriched beta phase also achieved a fixed composition regardless of the initial niobium content of the alloy. These data are compared in Fig. 11 with compositions of the enriched beta phase produced by precipitation of promonotectoid alpha. It is apparent that an $\omega + \beta$ transus line

*If there were no changes in interatomic spacing, the axial ratio would be 0.612, a condition observed in titanium alloys (8, 10).

FIG. 10-11. DETERMINATION OF BETA TRANSUS LINES FROM REFERENCE 14.

exists and is analogous in all respects to the $\alpha + \beta$ transus line. The metastability relative to alpha of the omega-beta equilibrium is emphasized by the lower niobium content of the ω - β transus.

The ω - β transus has special significance in connection with the reversion and retrogression phenomena that occur when an aged alloy is reheated to higher temperatures in the $\alpha + \beta$ range. As in many other age hardening reactions, omega will revert back to beta upon reheating to temperatures well below the $\alpha + \beta$ equilibrium boundary (5, 11). The results of a few experiments conducted on these alloys are recorded on Fig. 11 where it is demonstrated that partial reversion (retrogression) occurs upon reheating to a temperature below the $\omega + \beta$ transus and complete reversion to the original beta takes place upon heating to a temperature above this transus. Thus, the $\omega + \beta$ transus has the same significance for the metastable omega phase as does the $\alpha + \beta$ transus for the stable alpha phase.

Diffusionless Formation of Omega

Omega formed by isothermal transformation or aging clearly requires compositional readjustments and occurs at the low rates dictated by diffusional processes. At the lower niobium levels, however, the formation of omega during cooling cannot be suppressed even by drastic quenching. Thus, omega also can form in a diffusionless manner. Omega formed in this way will be termed athermal

omega. The variation of the lattice parameters of athermal omega with alloy content - Fig. 10 - reveals that this form of omega inherits the composition of the original beta thus providing striking confirmation of the diffusionless nature of the transformation. Although this transformation clearly is diffusionless, hot stage metallographic studies have not revealed the surface tilts that characterize diffusionless transformations of the martensitic type. Formation of omega apparently does not involve the parallel displacement in the same crystallographic direction of many atomic planes such as that which produces the surface tilts observed in true martensitic transformations.

The temperature for initiation of the omega reaction during cooling (ω_s) cannot be determined by metallographic techniques. Thus, less direct methods must be adopted to determine this temperature. The hardening or volumetric changes that accompany direct isothermal transformation provide one means for determining ω_s . Figs. 12 and 13 present hardness and dilation data for the 12% niobium alloy. At temperatures below ω_s , an immediate hardening and contraction results from the aging and continued formation of omega; whereas, an induction period precedes hardening or contraction at temperatures above ω_s . Thus, Fig. 12 reveals that ω_s lies between 325 and 350°C in the 12% niobium alloy. X-ray diffraction and electrical resistivity techniques have provided alternate means for determining ω_s .

FIG. 10-12. DILATION CURVES FOR ISOTHERMAL AGING OF THE Zr-12% Nb ALLOY

FIG. 10-13. HARDNESS ISOTHERMS FOR THE 12% Nb ALLOY (LOW TEMPERATURE AGING).

The ω_s temperature is lowered by increasing alloy content as illustrated in Fig. 14 and comparison of Figs. 11 and 14 reveals that

ω_s is well below the $\omega + \beta$ transus. Tentatively, it is proposed that ω_s represents that temperature at which ω and β of the same composition have equal free energies.

Reversibility of Athermal Omega

The diffusionless transformation of beta to omega takes place reversibly with virtually no hysteresis. This interesting aspect of the transformation can be observed most clearly in the 17.5% and 25%Nb alloys where ω_s is low enough to prevent loss of the supersaturated state by partition of niobium to the surrounding beta. Electrical resistivity and x-ray intensity measurements have been used to explore this reversibility of the omega reaction.

The temperature-resistivity behavior of the 17.5%Nb alloy is presented in Fig. 15. Here, resistance was measured as the sample was cooled from room temperature to -190°C and upon reheating to $+220^\circ\text{C}$. Heating and cooling curves superimpose and the resistivity behavior is characterized by a negative temperature coefficient of resistivity at subzero temperature - a behavior also exhibited by Ti-V alloys in a narrow composition range near 20%V (11).

The negative temperature coefficient of resistivity results from the diffusionless formation of omega as the temperature is lowered.

FIG. 10-14. T_s AS A FUNCTION OF COMPOSITION.

FIG. 10-15. ELECTRICAL RESISTANCE OF AS-QUENCHED 17.5% Nb ALLOY.

This is demonstrated in Fig. 15 where the intensity distribution of the (002) omega reflection at room temperature is compared with that at -196°C . The increase in intensity with reduction in temperature is striking.* Since the peak position does not shift significantly with temperature, the change in peak intensity was studied as temperature was varied. For this purpose, liquid nitrogen was dripped on the sample while mounted on the x-ray spectrogoniometer.

The intensity appeared to respond instantaneously to change of temperature - increasing as the temperature was lowered to -196°C and returning to its original value as the temperature returned to room temperature. Any hysteresis was exceptionally small-probably not exceeding $5-10^{\circ}\text{C}$. Thus, the formation of athermal omega takes place in a thermally reversible manner. This reversibility is further confirmed by the superposition of the cooling and heating curves in Fig. 15. Note also that the 17.5% niobium alloy exhibits a normal, positive temperature coefficient of resistivity at temperatures above approximately 130°C . X-ray intensity studies indicate that the omega phase disappears at this same temperature so that ω_s for the 17.5% alloy is approximately 130°C .

*Intensities of the beta reflections were lower at -196°C than at room temperature thus indicating that the increased intensity in Fig. 16 truly reflects an increase in the amount of omega.

FIG. 10-16. INTENSITY OF THE $(00\cdot2)\omega$ SPOT IN THE QUENCHED 17.5% Nb ALLOY AT ROOM TEMPERATURE AND -196°C .

At temperatures near or below room temperature, omega in the quenched 12% niobium alloy exhibited the same, instantaneous reversibility observed in the 17.5% niobium alloy. However, rapid dissociation (tempering) of the athermal omega by partition of niobium to the surrounding beta was encountered on heating to higher temperatures. The resulting reduction in niobium content of omega increases its ω_s temperature (Fig. 14) and thus raises the temperature for complete reversion. This retention of omega as a result of "tempering" produces significant differences in the response of low niobium alloys (less than 17% niobium) to isothermal and quench aging treatments at temperatures between ω_s and the $\omega + \beta$ transus. For example, Fig. 13 demonstrates that an instantaneous hardening accompanies aging of the 12%Nb alloy at 400°C, whereas, a significant induction period precedes isothermal transformation at this temperature. The instantaneous response to aging results from the presence of omega inherited from the prior quench to room temperature while the induction period that precedes isothermal transformation reflects the need for "nucleation" of omega since this temperature is above ω_s (335°C).

HIGH TEMPERATURE REACTIONS

The transformation processes that occur at high temperatures, i. e., above approximately 450°C, are, in general, those that would

be anticipated from the equilibrium diagram. Two distinct decomposition mechanisms - one based on the precipitation of promonotectoid alpha and the other on a cellular or pearlitic reaction - have been observed.

Promonotectoid Alpha Reaction

The initial decomposition of the 12% and 17.5%Nb alloys was accomplished by precipitation of promonotectoid alpha. While this transformation generally was initiated at beta grain boundaries, uniform precipitation throughout the grain took place rapidly - Fig. 17. Since these alloys were relatively coarse grained, diffraction lines were not continuous but consisted of distinct spots. The diffraction lines from the alpha phase (Fig. 20) also were spotty reflecting the lattice relationship between alpha and the beta matrix expected from the widmanstatten character of the microstructure. Simultaneously with the appearance of alpha the beta lines became diffuse and, after long aging times, displaced in the direction of increased niobium content. The compositions of the enriched beta phase were estimated from these stabilized positions of the beta lines and are entered on Fig. 11 where it is apparent that the composition of beta is dictated by the metastable extrapolation of the $\alpha + \beta$ transus line. The promonotectoid alpha achieves a metastable equilibrium with beta based on the influence of alloy content on the allotropic transformation of beta to-alpha. This

AGED 550°C 1HR, BRINE QUENCH
ALPHA + ENRICHED BETA.

FIG. 10-17. Zr-12% Nb ALLOY (1000 X)
900°C 1HR, BRINE QUENCH
PLUS AGING TREATMENT
ELECTROLYTIC POLISH.

enriched beta phase decomposes eventually to yield additional alpha and the β_{Nb} phase expected from the equilibrium diagram. However, the fine distribution of alpha resulting from the promonotectoid reaction has prevented metallographic study of this aspect of the decomposition sequence.

The formation of promonotectoid alpha exerts significant effects on hardness of the 12% and 17.5% alloys - Fig. 18. The hardening observed in the 17.5%Nb alloy probably results primarily from the extremely fine distribution of alpha. The loss in hardness of the 12% niobium alloy results from the influence of enrichment of beta on the ω_s temperature - Fig. 14. Thus, as the beta phase becomes enriched beyond approximately 17%Nb omega no longer forms as the alloy is cooled from the transformation temperature to room temperature which results in the loss in hardness.

Cellular Decomposition

The microstructure of the 25% niobium alloy partially transformed at 550°C is illustrated in Fig. 19. The nodular structure initiated at beta grain boundaries reveals that this alloy can transform by a cellular reaction analogous to that in many age hardening systems (12-14) and to the formation of pearlite in steel. Significantly, the cellular reaction has been observed in these zirconium-niobium alloys at temperatures both above and below the monotectoid although

FIG. 10-18. HARDNESS ISOTHERMS FOR HIGH TEMPERATURE AGING.

AGED 550°C 24 HR, BRINE QUENCH

AGED 550°C, 48 HR, BRINE QUENCH

FIG. 10-19. Zr-25 %Nb ALLOY (500 X)
900°C 1HR, BRINE QUENCH
CHEMICAL POLISH

the structure of the cells is different in the two temperature ranges.

Above the monotectoid (610°C) the cells consist of lamellae of the B_I and B_{II} phases as revealed by x-ray studies. The high niobium beta in cells formed at 625°C contained approximately 90% niobium as expected from the equilibrium diagram. Thus, the cellular reaction produces essentially complete segregation at temperatures above the monotectoid.

Immediately below the monotectoid, the cells consist of lamellae of alpha and a niobium rich beta phase. The low angle portion of a Debye-Scherrer pattern of a sample partially transformed at 600°C is presented in Fig. 20. Note that the diffraction lines from the original beta remain sharp and spotty thus indicating that no long range concentration gradients, such as those associated with the precipitation of promonotectoid alpha, are established in the beta matrix. Virtually all of the segregation is accomplished in the advancing cell boundary. The sharp and continuous reflections from the alpha and β_{Nb} phases also are significant and reveal that the orientations of alpha and β_{Nb} are essentially random. This is a characteristic of cellular reactions (14).

In contrast to the behavior above the monotectoid temperature, the cellular reaction at temperatures below the monotectoid did not produce complete segregation. Specifically, the beta phase (β_{Nb}) was

enriched to approximately 75% Nb rather than 90% as expected from the equilibrium diagram. Such incomplete segregation has been observed in other cellular reactions (13).

In spite of the hypermonotectoid nature of the 25%Nb alloy, promonotectoid alpha precipitates in this composition in much the same way that it does in the lower niobium alloys. This occurs at temperatures below the extrapolated $\alpha + \beta$ solvus line (approximately 580°C according to Fig. 11) where beta is supersaturated with respect to alpha. The character of the diffraction lines in Debye-Scherrer patterns provides the clearest evidence for this reaction sequence. Samples transformed at 475 to 550°C, exhibited the diffuse retained beta and spotty alpha lines characteristic of the promonotectoid reaction in the 12% and 17.5%Nb alloys (Fig. 20) rather than the sharp retained beta and continuous alpha and beta niobium lines associated with the cellular reaction (Fig. 20).

As indicated on the TTT diagram (Fig. 9), the direct precipitation of promonotectoid alpha from beta competes with the cellular reaction at temperatures in the range 475 to 575°C. Here, the promonotectoid reaction exhausts the free energy driving force for cell propagation and mixed microstructures consisting of alpha platelets and cellular nodules exist at the completion of transformation as revealed by disappearance of beta of the original composition from the x-ray

FIG. 10-20. LOW ANGLE PORTION OF A DEBYE PATTERN FROM THE 25% Nb ALLOY QUENCH-AGED FOUR DAYS AT 600°C. (FILTERED COPPER K_{α} RADIATION).

FIG. 10-21. LOW ANGLE PORTION OF A DEBYE PATTERN FROM THE 17.5% Nb ALLOY ISOTHERMALLY AGED TWO DAYS AT 500°C. (FILTERED COPPER K_{α} RADIATION).

diffraction pattern.

The cellular reaction observed in the 25% niobium alloy represents one method for accomplishing in a discontinuous or heterogeneous manner the segregation required by the solubility gap. The behavior of other systems exhibiting a solubility gap (15, 16) would suggest that this segregation also should be accomplished in a homogeneous manner at lower temperatures. In fact, it is attractive to assume that a segregation of beta into high and low solute regions precedes the isothermal formation of omega at temperatures above ω_s and plays an important role in the nucleation process. While no evidence for this segregation could be found in the present study, it has been observed in certain titanium alloys (17).

SUMMARY AND CONCLUSIONS

The subcritical decomposition of beta in zirconium-niobium alloys involves the formation of the equilibrium phases alpha and β_{Nb} at reaction temperatures above approximately 500°C and formation of the metastable omega phase at lower temperatures. The high temperature reactions take place by two fundamentally different mechanisms. A cellular reaction was observed in the hypermonotectoid alloy and takes place at temperatures both above and below the monotectoid. This reaction represents one method for accomplishing the segregation required by the solubility gap.

Hypomonotectoid alloys decompose initially by the formation of alpha zirconium. This direct precipitation of alpha from beta also occurs in the hypermonotectoid alloy at reaction temperatures below the metastable extrapolation of the $\alpha + \beta$ transus.

The omega phase which appears at lower temperatures can form in either a diffusionless or a diffusion controlled manner. The diffusionless formation occurs as the temperature is lowered below a critical temperature determined by composition. This temperature has been designated ω_s and is lowered by increasing niobium content. The diffusionless formation of omega appears to be thermally reversible and results in a negative temperature coefficient of electrical resistivity.

The isothermal formation of omega establishes a metastable equilibrium between an impoverished omega phase and an enriched beta phase. The $\omega + \beta$ transus associated with this equilibrium has been identified and employed to rationalize the retrogression characteristics of this transformation.

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THE EFFECT OF HEAT TREATMENT ON THE MECHANICAL PROPERTIES
OF THE ZIRCONIUM - 2 1/2% NIOBIUM ALLOY

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The Effect of Heat Treatment on the Mechanical Properties of the Zirconium - 2 1/2% Niobium Alloy

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Introduction

It is the purpose of this report to describe one aspect of the work carried out at R.M.L. Culcheth in support of the development programme on water reactors. It has been demonstrated that a zirconium alloy containing about 2 1/2% niobium is a possible alternative pressure tube material to Zircaloy-2 (8). One advantage of the niobium alloy is that it is capable of being heat-treated to higher strengths than Zircaloy-2 and therefore it is possible to employ thinner pressure tubes with a consequent saving of neutrons.

It was known from the above work that the heat treatment of this alloy consisted of a high temperature quench followed by an ageing treatment. In such a heat treatment there are many variables and it is important to be able to optimise heat treatment conditions to give the best combination of properties in the final material. In the programme of work described in this report, a wide range of heat treatment variables have been covered including quenching temperature, quenching rate, ageing temperature and ageing time. On the basis of this work a specific heat treatment schedule is recommended.

The Constitution of Zr-Nb Alloys

A number of phase diagrams at the low Nb end of the Zr-Nb system have been reported. (1, 2, 3, 4, 5). They all agree that Nb acts as a beta stabilising element and some of the diagrams suggest a eutectoid at about 600°C and 12-20% Nb, but the diagram given by Richter (5) is complicated by ternary characteristics due to the presence of oxygen. The solid solubility of Nb in alpha zirconium is variously quoted to be 0.5 to 6.5%, the most recent determination (5) being about 2%. The decreasing solubility of Nb in alpha zirconium below 600°C indicates age hardening potentialities.

For low niobium contents, rapid quenching from the beta phase results in a transformation to martensitic alpha. Quenching higher niobium alloys (more than 5%) can result in the formation of an omega phase, which is a transition phase between alpha and beta and which is highly undesirable because of

the brittleness which it tends to produce. The omega phase is unlikely to occur in alloys containing only 2 1/2% Nb.

The form of the diagram is modified by the presence of oxygen. Its most important effect in low niobium alloys is to increase the beta/alpha + beta transition temperature.

Metallographic work associated with the present investigation showed that retained alpha was present in the martensitic matrix in specimens quenched from below 950°C and pure martensite only above this temperature. This may be taken as the beta/alpha + beta transition temperature for the particular material used in this investigation. In the absence of oxygen this temperature would be expected to be below 880°C.

Material Employed

The present work has been carried out entirely on one batch of nominally 2 1/2% Nb material supplied by I.M.I. Ltd. in the form of hot rolled 1/2 in. plate. The hot rolling was carried out at 750°C and after rolling the 1/2 in. plate was annealed at 750°C for about 30 minutes.

An analysis of the important elements in the original 1/2 in. plate is as follows:-

Nb	2.7 - 2.9%
O ₂	1400-1600 p.p.m.
Al	<50 p.p.m.
Fe	600 p.p.m.
Ti	<50 p.p.m.
Hf	60 p.p.m.
Ni	<40 p.p.m.
N ₂	50 p.p.m.
H ₂	<10 p.p.m.

The Effect of Quenching Variables on Tensile Properties

When this investigation began, it was known that the attainment of maximum strength in this type of alloy was brought about by a high temperature quench to develop a martensite structure followed by an ageing treatment at about 500°C. Since the major part of the strengthening is developed during the high temperature quench it was important to optimise quenching conditions.

The two variables studied were quenching temperature and cooling rate. The importance of quenching temperature lay in the question as to whether to quench from the pure beta or the alpha + beta field, the latter being favoured by A.E.C.L. as a

means of preventing the possible deleterious effects of beta grain growth. The importance of cooling rate in this type of system is to obtain a swift enough rate to obtain a purely martensitic transformation and, as became clear at a later stage, to avoid precipitation during quenching.

Since it was intended to determine tensile properties at 300°C on No.12 Hounsfield Tensometer test pieces, blanks were cut from the 1/2 in. plate having dimensions 0.45 in. diameter x 1 3/4 in. long. These were heated in argon for a period of 1/2 hour at temperatures between 875 and 1000°C and then quenched into either water or oil. Heat-treating blanks and then machining out the tensile specimen avoided any surface contamination caused by the heat treatment.

Figs 1, 2 and 3 give the 300°C tensile properties of water and oil quenched material as a function of quenching temperature. In the case of water quenched material, a value of 88,000 p.s.i. for the U.T.S. was obtained which is independent of quenching temperature, but there appears to be a distinct increase in Reduction of Area with increasing temperature. In the oil quenched case a material of variable quality was obtained, having U.T.S. values up to 105,000 p.s.i. at the higher quenching temperature. The values for Reduction in Area were variable but on the whole were lower than in the water quenched material, and sometimes as low as 20%.

The difference in the properties of the water and oil quenched materials could only be caused by the difference in cooling rate and therefore in an attempt to find an explanation the effect of cooling rate on hardness was determined. This involved the measurement of very fast cooling rate employing a thermocouple at the centre of specimens and a quick response potentiometer. Cooling media included a stream of air, hot and cold oil and hot and cold water. The cooling rate quoted in Figure 4 is the mean rate between 1000°C, the quenching temperatures, and 500°C. Figure 4 shows that the hardness increases to a maximum at 100°C/sec., corresponding with quenching a tensile blank into cold oil, but at higher rates decreases to a constant value. Quenching a tensile blank into cold water corresponded to a cooling rate of 140°C/sec.

One obvious explanation for this behaviour is that at the highest quenching rates pure martensite is formed but at the slower rates there is sufficient time for some type of precipitation to occur at the same time as martensite, thus increasing the hardness. At even slower rates martensite will not form, thus resulting in a lower hardness.

FIG. 1. ZR - 2½% Nb. MECHANICAL PROPERTIES AT 300°C. vs.
QUENCHING TEMPERATURE.
WATER QUENCHED.

FIG. 2. MECHANICAL PROPERTIES AT 300 °C. AFTER OIL QUENCHING.

FIG. 3. MECHANICAL PROPERTIES AT 300 °C. AFTER OIL QUENCHING.

FIG. 4. ZR - 2 $\frac{1}{2}$ % Nb. HARDNESS vs. COOLING RATE.

The Effect of Ageing

Since it was known that quenched material could be further strengthened by ageing at 500°C (8), the next stage in the present programme was to determine the effect of ageing variables and their relationship to quenching variables.

Age-hardening curves for 1000°C water quenched material aged in evacuated silica capsules at 400, 450, 500 and 550°C for periods up to 100,000 minutes are given in Figure 5. It is clear that the maximum response from 254 to 290 VPN is obtained at 500°C and below but that the quickest response is at 500°C and therefore this temperature is to be preferred. Figure 6 shows how the response to ageing varies with quenching temperatures between 880° and 1000°C from which it appears that the best response is obtained on ageing after the 1000°C quench.

The effect of ageing time at 500°C on tensile properties at 300°C after water quenching from 1000 and 880°C are given in Figures 7 and 8. There is a clear increase in U.T.S. from 87 to 95,000 p.s.i. in the case of the 1000°C quench and a comparable increase in the case of the 880°C quench, which agrees with the response noted in the hardness values after 300 minutes ageing. At both water quenching temperatures there is a fall in Reduction of Area and elongation values at the larger ageing times associated with the general increase in strength and hardness.

The corresponding results for 1000°C oil quenched material are given in Figures 9 and 10. There appears to be a gradual decrease in the U.T.S. value with ageing time from the as quenched value of 101,000 p.s.i. and perhaps a small increase in Reduction of Area but as with the quenched material, there is a large spread in results. These results are consistent with those of hardness tests on oil quenched material in which it was found that little or no hardening occurred in this material on ageing at 500°C. This agrees with the previous suggestion that precipitation has already occurred either partially or fully during oil quenching.

It may be concluded from these results that the most consistent material is obtained by water quenching and ageing rather than from a slower cool which allows precipitation to occur.

Quenching from 1000°C is preferred to lower temperature quenching on the grounds of better response to ageing and superior ductility. During ageing, an optimum combination of strength and ductility may be obtained by a 5 hour treatment at 500°C.

FIG. 5. ZR - 2 $\frac{1}{2}$ % Nb. AGEING CHARACTERISTICS AFTER 1000 °C WATER QUENCH.

FIG. 6. ZR - 2½% NB. EFFECT OF QUENCHING TEMPERATURE ON AGEING AT 500°C.
WATER QUENCH.

FIG. 7. ZR - 2 1/2 % Nb. MECHANICAL PROPERTIES AT 300°C. AFTER AGEING AT 500°C.

FIG. 8. ZR-2 $\frac{1}{2}$ % Nb. MECHANICAL PROPERTIES AT 300°C. AFTER AGEING AT 500°C.

FIG. 9. MECHANICAL PROPERTIES AT 300°C AFTER AGEING AT 500°C. -OIL QUENCHED.

FIG. 10. MECHANICAL PROPERTIES AT 300°C AFTER AGEING AT 500°C. - OIL QUENCHED.

Impact Properties

The heat treatment variables which have been considered in relation to Charpy impact strength at 300°C are quenching temperature, time at the quenching temperature, ageing time and rate of cooling. The first two variables are of importance in relation to the beta grain size at the quenching temperature.

Figure 11 gives the 300°C Charpy impact values for water and oil quenched materials, quenched between 875 and 1000°C after holding at these temperatures for 30 minutes. The strengths lie within the range 34-53 ft. lb. and appear to be independent of quenching temperature and rate of cooling. Indeed, the value for slowly (furnace) cooled material is very much the same at 50 ft. lb.

Values for material held for up to 1000 minutes at 1000°C prior to quenching in oil or water are given in Figure 12. Again the values at 300°C are practically independent of holding time at about 40-50 ft. lb., emphasising the previous results at various quenching temperatures, and showing that the high temperature beta grain size has no significant effect. That the beta grain size had increased during the 1000°C treatment can only be inferred and not directly measured as only a martensitic structure was visible in these specimens.

The way in which ageing at 500°C after oil and water quenching from 1000 to 880°C affects the impact strength is shown in Figure 13. The 1000°C water quenched material has a strength of 50-60 ft.lb. independent of ageing time up to 1200 minutes. The value of 71 ft.lb. shown by material aged for 300 minutes after oil quenching from 1000°C appears to be anomalously high. Comparison of Figures 11 and 13 indicates that the 880°C quenched materials decrease in strength from about 42 to 32 ft. lb. on ageing for over 300 minutes.

Finally, it must be emphasised that the above results have been obtained on one specific batch of material. Recent results from current work on a second batch of material suggest that there may be significant variations in impact values in different batches of material. The cause of this is being investigated.

Fatigue

In a pressure tube, possible fatigue stresses could arise in the first case by pressure variations within the tube and secondly by thermal cycling. The amplitude and frequency of these fatigue stresses are not precisely known and therefore

FIG. 11. ZR-2½% Nb. CHARPY IMPACT TESTS AT 310°C. - EFFECT OF QUENCHING TEMPERATURE AND COOLING RATE.

FIG. 12. ZR - 2½ %Nb CHARPY IMPACT RESULTS AT 300°C. - EFFECT OF TIME AT QUENCHING TEMPERATURE.

FIG. 13. ZR - 2 $\frac{1}{2}$ % Nb. CHARPY IMPACT RESULTS AT 300°C. - EFFECT OF AGEING TIME.

no attempt has been made to simulate them for testing the 2 1/2% Nb alloy.

So far the fatigue work has consisted of determining the S/N curve for material in the preferred heat treated condition (1000°C WQ + 5 hours at 500°C).

The tests were carried out on an Amsler machine operating at 4000 cycles/min., the push/pull stress being applied on a specimen 0.2 in. diameter by 0.8 in. gauge length. The test temperature was 300°C and an attempt was made to reduce oxidation by passing a slow bleed of argon through the furnace.

The S/N curve is given in Figure 14 from which it can be seen that the fatigue limit is about 30,000 p.s.i., which is 1/3 of the tensile strength at this temperature.

Also given on Figure 14 are a few results for 880°C WQ and aged material, which indicate that there is no significant difference in fatigue strength between this and the corresponding 1000°C quenched material.

Creep Testing

In order to reduce the number of creep tests, it was decided to make a direct comparison of materials in the two most favoured heat treated conditions over a range of stresses and at one temperature. The temperature chosen was 310°C as the anticipated highest temperature that would be attained in the pressure tube of a saturated S.G.H.W. reactor. The four stresses chosen were 30, 45, 60 and 75,000 p.s.i. The two heat treatments selected were 1000°C WQ + 5 hours at 500°C and 880°C WQ + 5 hours at 500°C. The tests are currently being carried out in NPL type creep testing machines in a dynamic vacuum of 10^{-4} cm Hg; the specimens have a gauge length of 1 1/2 in. and a diameter of 3/16 in.

To the end of July 1962, the tests have completed about 2000 hours with resultant creep curves given in Figures 15 and 16.

It is early yet to present definite conclusions from these curves but preliminary ones are discussed below.

As regards the curves for the three highest stresses, the extent of primary creep appears definitely to be greater in the 880°C WQ material. On the other hand primary creep appears to be smaller in the material at 30,000 p.s.i. but this may be an anomolous result because of the displacement of the zero in the

FIG. 14. FATIGUE BEHAVIOUR OF ZIRCONIUM - 2½% NIOBIUM ALLOY TESTED AT 300°C.
 4,000 CYCLES PER. MINUTE.

FIG.15. CREEP OF ZR-2 1/2 % Nb. AT 310°C. - 1000°C. WATER QUENCH. 500°C. 5L.

FIG. 16. CREEP OF ZR - 22% Nb. AT 310°C. - 880°C. WATER QUENCH. 500°. 5b.

particular curve, perhaps due to extensometer errors. A noticeable feature of the two low stress curves, especially that of the 1000°C WQ material, is the temporary increase in strain rate occurring at about 2000 hours. This type of jog is not unique as it has been previously observed in Zircaloy-2 (6) and certain magnesium alloys (7). There is as yet no satisfactory explanation of the phenomenon.

Latest values for creep rates are as follows (the ones for the 30,000 p.s.i. stress are after the jog).

Stress p.s.i.	1000°C WQ and aged %/hour	880°C WQ and aged %/hour
30,000	10 ⁻⁶	4 x 10 ⁻⁶
45,000	1.3 x 10 ⁻⁵	1.5 x 10 ⁻⁵
60,000	2.5 x 10 ⁻⁵	3 x 10 ⁻⁵
75,000	1.0 x 10 ⁻⁴	1 x 10 ⁻⁴

Metallography

The slowly cooled alloy has a Widmanstatten structure (Figure 17) which consists of alpha grains formed from the high temperature beta grains. This is usually associated with rapidly cooled, high oxygen zirconium.

Water quenching the alloy from 1000°C results in a typical martensitic structure with no second phase present (Figures 18 and 19). Ageing this material at 500°C results in the appearance of a fine precipitate after 5 hours (Figure 20) and a coarser precipitate after 100 hours (Figure 21).

Water quenching from temperatures below 1000°C results in the appearance of retained alpha. This is shown at the original beta boundaries after a 950°C water quench (Figure 22). After an 875°C quench (Figure 23) retained alpha is present profusely in regular orientations and there is little evidence of the martensitic structure.

On oil quenching a fine structure is formed which is not resolvable by the optical microscope (Figure 24). Figure 25 shows the electron micrograph of the structure and it appears to show a Widmanstatten pattern which may be caused by a second phase precipitated on regular crystallographic planes.

An attempt has been made to identify the precipitates observed by examination of the electron diffraction patterns obtained from carbon extraction replicas. So far, positive identification has been possible in the case of 1000°C WQ

material aged for 100 and 1700 hours. The lattice parameters indicate that the precipitate is essentially niobium but the extent of zirconium in solid solution is not certain.

An attempt to identify the precipitate produced during oil quenching is currently being carried out.

Discussion

On the basis of the present results, two points stand out clearly. First, that in material of the composition employed, it is essential to quench faster than a critical rate in order to obtain consistent properties and a good ageing response. Secondly that an ageing temperature of 500°C gives a sufficiently rapid increase in strength together with good ductility for ageing times of about 5 hours. It is realised, however, that such factors as intermediate cold work may affect ageing response and this is the subject of current work.

The important heat treatment condition which is debatable is the optimum quenching temperature. Theoretically it would be expected that material quenched from the pure beta range would be harder and stronger than material quenched from the alpha plus beta range simply by virtue of it being a pure martensitic quench, i.e. no retained alpha. This is apparently not borne out if one considers the tensile values (Figure 1) which are independent of quenching temperature. On the other hand, the creep results so far would indicate that the 1000°C quenched material suffers less primary creep than 880°C quenched material. The tensile results would also indicate that the higher temperature quenched material has superior ductility.

As far as the effect of ageing is concerned, the response is better in the 1000°C quenched material than in 880°C quenched material as borne out by both hardness and tensile curves, but there is no significant difference after a 5 hour at 500°C treatment.

Impact values appear peculiarly insensitive to heat treatment conditions although there is some evidence that 1000°C quenched and aged material has a higher impact strength than the corresponding 880°C quenched material. It must be emphasised again, however, that these are preliminary results obtained on one batch of material and that results on a second batch of material would indicate no significant difference.

In conclusion, it must be remembered that the differences

FIG. 11-17

SPECIMEN WATER-QUENCHED
FROM 1000°C.

x150

FIG. 11-18

ELECTRON MICROGRAPH
OF SPECIMEN WATER-
QUENCHED FROM 1000°C.

x4000

FIG. 11-19

ELECTRON MICROGRAPH
OF SPECIMEN WATER-
QUENCHED FROM 1000°C
AND AGED 5 HOURS AT
500°C.

x4000

FIG. 11-20

ELECTRON MICROGRAPH
OF SPECIMEN WATER-
QUENCHED FROM 1000°C
AND AGED 100 HOURS AT
500°C.

x5000

FIG. 11-21

SPECIMEN WATER-
QUENCHED FROM 950°C.

x150

FIG. 11-22

WATER QUENCHED FROM
875°C.

x150

FIG. 11-23

OIL QUENCHED FROM
1000°C.

x150

FIG. 11-24

ELECTRON MICROGRAPH
OF SPECIMEN OIL-
QUENCHED FROM 1000°C.

x20000

in properties exhibited by material quenched from 880°C and 1000°C are quite small and it is debatable whether they are significant when considering that in a production process 1000°C quenching may be significantly more difficult than 880°C quenching.

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Compiled by
H. H. Klepfer

November 30, 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

UNITED STATES - EURATOM JOINT RESEARCH AND DEVELOPMENT PROGRAM

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

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VOLUME II

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VALLECITOS ATOMIC LABORATORY
GENERAL ELECTRIC
ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

THE ROLE OF DEFORMATION TWINNING IN THE PLASTIC
DEFORMATION OF ZIRCONIUM

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The Role of Deformation Twinning in the Plastic Deformation of Zirconium

by

R. E. Reed-Hill*

Introduction

Under the conditions of temperature and strain rate of normal usage, cubic metals may be considered to deform almost exclusively by processes related to slip. Since, in the past, the majority of useful metals have been cubic in structure, it is only natural that the greatest research efforts in the field of plastic deformation have been on investigations of the phenomena of slip. One of the results of this concentration of emphasis is that the study of mechanical twinning as a means of deformation has been more or less neglected, and the metallurgical phenomena associated with twinning are, for the most part, poorly understood. In hexagonal metals, however, deformation by twinning is often very important. This is particularly true in the case of polycrystalline zirconium which has a very limited capability of deformation by slip since a zirconium crystal possesses only three major slip systems with all slip directions lying in a single plane (the basal plane).⁽¹⁾ The good ductility which polycrystalline zirconium normally exhibits under most conditions of deformation is undoubtedly related to the fact that it has

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a multitude of possible twinning habits. It is evident, therefore, that a study of twinning phenomena in zirconium is necessary in order to lay the groundwork for an understanding of its deformation textures. Twinning is also probably closely connected to the observed recrystallization textures of zirconium since it is known that twin intersections may serve as recrystallization nuclei.⁽²⁾ This furnishes an additional incentive for a study of deformation twinning in zirconium. Finally, there are indications^(3,4) that the role of twinning in the fracture of zirconium may be very important and should be investigated.

Experimental Procedures

All specimens in the work reported were deformed in tension on an Instron machine. A 0.130 inch diameter by 1.25 inch long cylindrical gage section was employed and the specimens were machined from a 5-inch wide by 1/2-inch thick plate. The material was annealed Wah Chang arc melted sponge zirconium with an ASTM grain size 4 containing, in parts per million, 380 Fe, 880 O, <40 Hf, 32 N, and <5 H. In order to provide a gage section initially free of twins, acid machining was used as the final step in forming the gage sections. At least 30 thousandths of an inch were removed from the surfaces in this manner.

Two basic specimen orientations were used. In one, specimens were cut from the plate with their axes parallel to the rolling direction. These are designated longitudinal

specimens. The others were cut with axes normal to the rolling direction and are designated as transverse specimens. The metal of the plate has a typical zirconium texture with a strong alignment of the basal planes of the grains parallel to the rolling direction, while, at the same time, the basal planes are rather uniformly distributed about this direction. Because of this basic texture, almost every grain of a longitudinal specimen is favorably aligned for deformation by $\{10\bar{1}0\}$ prism slip. In a transverse specimen, on the other hand, only a fraction of the grains are ideally oriented for slip. These are the grains whose basal planes are parallel to the rolling plane of the plate. Grains with basal planes steeply inclined to the rolling plane are, in general, unfavorably aligned for slip in a transverse specimen because the $\langle 11\bar{2}0 \rangle$ slip directions (of the prism slip planes) are nearly normal to the tensile stress axis.

Specimens were examined metallographically, primarily on longitudinal sections, using surfaces which were first chemically polished and then anodized according to a modification of the procedures recommended by Picklesimer.⁽⁵⁾ All photographs were made using polarized light.

The Twinning Modes in Zirconium

The known twinning modes for zirconium are listed in Table 1. The twinning elements have been experimentally measured for three of these twins and are listed in the table.

TABLE I - TWINNING ELEMENTS IN PURE ZIRCONIUM^(6,7)

Twinning or First Undistorted Plane K_1	Twinning Shear Direction η_1	Second Undistorted Plane K_2	η_2	Magnitude of Shear
$\{10\bar{1}2\}$	$\langle 10\bar{1}1 \rangle$	$\{10\bar{1}2\}$	$\langle 10\bar{1}1 \rangle$	0.167
$\{11\bar{2}1\}$	$\langle 11\bar{2}6 \rangle$	$\{0002\}$	$\langle 11\bar{2}0 \rangle$	0.63
$\{11\bar{2}2\}$	$\langle 11\bar{2}3 \rangle$	$\{11\bar{2}4\}$	$\langle 22\bar{4}3 \rangle$	0.225
$\{11\bar{2}3\}$	-	-	-	-

The sense of shear for a twinning mode is determined by the angle between the twinning plane K_1 and the second undistorted plane K_2 ; for, as shown in Fig. 1, K_2 rotates about its intersection with K_1 during the formation of a twin so as to form the same angle with K_1 before and after the shear. The positions of both K_1 and K_2 relative to the basal plane, as well as the angle between these two planes, are indicated in Fig. 2 for the three experimentally determined modes. In each case, the direction and sense of the twinning shear is shown, as well as an indication of the type of normal stress (tension or compression) which, when applied perpendicular to the basal plane of the crystal, will produce a shear stress of the proper sense along the twinning plane so as to yield a twin. The sketches of Fig. 2 show that both $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$ twins form under a tensile stress perpendicular to the basal plane. On the other hand, $\{11\bar{2}2\}$ twins are favored by a compressive stress normal to the basal plane.

FIG. 12-1. IN THE ABOVE DIAGRAM THE SPATIAL RELATIONS BETWEEN K_1 , K_2 , η_1 , AND η_2 ARE GIVEN. THE PLANE OF SHEAR IS THE PLANE PERPENDICULAR TO BOTH K_1 AND K_2 . η_2 IS THE DIRECTION FORMED BY THE INTERSECTION OF THE PLANE OF SHEAR WITH K_2 . NOTE THAT η_2 HAS TWO POSITIONS, ONE BEFORE AND ONE AFTER THE SHEAR.

$\{10\bar{1}2\}$ TWINNING

$\{11\bar{2}1\}$ TWINNING

$\{11\bar{2}2\}$ TWINNING

FIG. 12-2. THE NATURE OF THE TWINNING SHEAR IN THE THREE MOST IMPORTANT TYPES OF TWINS IN ZIRCONIUM.

Shear in $\{11\bar{2}1\}$ Twins

Attention is called to the fact that the values listed in Table I for K_2 and the twinning shear for $\{11\bar{2}1\}$ twins differ from those reported by Rapperport.⁽⁶⁾ The new values are based⁽⁷⁾ on a twinning shear measurement using the displacement of grain boundaries at positions where they are intersected by $\{11\bar{2}1\}$ twins. $\{11\bar{2}1\}$ twins tend to be parallel-sided, so that when a $\{11\bar{2}1\}$ twin intersects a grain boundary the total twinning shear may be applied to the boundary and transmitted into the adjoining grain. Examples of this phenomena may be seen in Fig. 3. Careful measurements of these grain boundary displacements, made on grains of known orientation, show beyond a reasonable doubt that the twinning shear is 0.63. Since the basal plane, when chosen as K_2 , has a predicted twinning shear of 0.63 and also yields a shear of the proper shear sense, the experimental results are in excellent agreement with this choice. It should be noted that the choice (0002) as K_2 is in agreement not only with recent Russian work⁽⁸⁾ but also with the earlier predictions of Hall.⁽⁹⁾

Morphological Features of $\{11\bar{2}1\}$ and $\{10\bar{1}2\}$ Twins

In discussing the phenomena of twinning in zirconium it is well to point out that the two most prominent types of twins, $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$, have different morphological features. As mentioned previously and as may be seen in

Fig. 3, $\{11\bar{2}1\}$ twins tend to have coherent boundaries. A second feature of this type of twinning is the frequent appearance of zig-zag twins.⁽¹⁰⁾ In general, this means that a single zig-zag shaped twin is formed from connected segments lying along two different crystallographic planes. Typical zig-zag twins are visible in Fig. 4. Several authors have indicated^(11,12) that zig-zag twinning and cross-slip are analogous in b.c.c. metals, for in cross-slip, cooperative glide occurs on two slip planes with a common slip direction, while in b.c.c. zig-zag twinning, cooperative twinning occurs on two twinning planes with a common shear direction. All known twinning modes in hexagonal metals have different shear directions so that two twinning planes with a common shear direction do not appear to exist. Zig-zag twinning in zirconium is therefore an interesting phenomenon because it has been proposed⁽¹¹⁾ that a common shear direction is an obvious geometrical necessity for b.c.c. cross-twinning to occur. In this regard, measurements made on the twins of Fig. 4 show that, while the shear directions of the cooperating planes are not colinear, the angles between them are usually small (16°); however in some isolated cases they may be larger (30°).

In contrast to $\{11\bar{2}1\}$ twins, $\{10\bar{1}2\}$ twins often tend to be highly lenticular or lens-shaped. This is particularly true when the twins are observed in heavily deformed metal. Many of these twins with non-coherent boundaries may be seen in Fig. 5 which represents the structure of a transverse specimen deformed to a strain of 29 pct. at room temperature.

FIG. 12-3. GRAIN BOUNDARY SHEAR DISPLACEMENTS AT POINTS WHERE $\{11\bar{2}1\}$ TWINS INTERSECT GRAIN BOUNDARIES AS SEEN ON THE SURFACE OF POLY-CRYSTALLINE PURE ZIRCONIUM SPECIMEN. 1500X

FIG. 12-4. ZIG-ZAG TWINNING INVOLVING CO-OPERATIVE DEFORMATION ON PAIRS OF $\{11\bar{2}1\}$ TWINNING PLANES. 1500X

FIG. 12-5. THE LENTICULAR SHAPE OF $\{10\bar{1}2\}$ TWINS WHICH IS OBSERVED AT LARGE STRAINS. 300 X

At small strains, however, the boundaries of $\{10\bar{1}2\}$ twins tend to be parallel-sided or coherent, as may be seen in Fig. 7 which shows the structure of a transverse specimen strained to only 0.21 pct. at room temperature.

Because of the basically different appearance of the two major forms of twins in zirconium it is often easy to distinguish them from each other, especially when the specimen has been subjected to a moderate amount of strain.

The Relationship of Twinning to the Specimen Orientation

Previously it has been mentioned that in a longitudinal specimen almost all of the grains are favorably aligned for deformation by slip. That deformation occurs primarily by slip in a specimen of this type can be clearly seen in Fig. 6 which shows the microstructure of a specimen deformed at room temperature to a strain of 25 pct. The lattice distortion associated with slip is clearly visible in almost all of the grains. It is further evident that twinning has occurred in only a minor fraction of the grains. Fig. 5, on the other hand, shows the microstructure of a typical transverse specimen also deformed at room temperature and to about the same strain (29 pct). This latter photograph shows that a large fraction of the grains in a transverse specimen undergo twinning when the specimen is deformed. It has also been generally observed that the twinned grains are those in which the basal plane is approximately normal to the stress axis. This fact can be readily verified with the polarizing micro-

scope. Thus, it is apparent that those grains, which are unfavorably aligned for slip, twin in order to conform to the macroscopic deformation of the specimen.

There is also good evidence for the assumption that twinning in grains unfavorably aligned for slip controls the flow pattern of the specimen as a whole. Thus, consider Figs. 7 and 8. The first shows the microstructure of a transverse specimen deformed to a very small strain; 0.21 pct. Twins are plainly visible in the structure, implying strongly that a measurable strain requires some twinning in the grains unfavorably aligned for slip. The second illustration Fig. 8, shows four stress-strain curves for zirconium specimens. One pair corresponds to tests made at room temperature on a longitudinal and a transverse specimen, while the other pair represents similar tests performed at 77°K. Attention is directed to these curves in the region of small strains. It is noteworthy that, at both test temperatures, the longitudinal specimens begin to yield or flow at much lower stresses than the transverse specimens. These are the specimens in which the grains deform primarily by slip. In contrast, transverse specimens require a much higher stress in order to initiate plastic deformation. Since the micrographic evidence (Fig. 7) shows that twinning in transverse specimens occurs simultaneously with the development of macroscopic strain, it is reasonable to assume that yielding occurs when the stress becomes high enough to nucleate twins in those grains unfavorably aligned for slip. This implies that the

FIG. 12-6. A LONGITUDINAL SPECIMEN DEFORMED TO 25 PCT. STRAIN. NOTE THE SMALL INCIDENCE OF TWINNING. 300X

FIG. 12-7. TWINS IN A TRANSVERSE TENSILE SPECIMEN
DEFORMED TO ONLY 0.21 PCT. STRAIN. 300X

FIG. 12-8. PURE ZIRCONIUM TENSILE STRESS-STRAIN CURVES. STRAIN RATE 0.016 in/min.

polycrystalline metal only flows when it becomes possible to produce macroscopic strain in all major components of the texture.

The close relationship between twinning and the total strain is also observed in longitudinal specimens, as well as in transverse specimens. In the longitudinal specimens, while it is true that almost all of the grains have their basal planes aligned nearly parallel to the stress axis, there are always a few grains with basal planes approximately normal to the stress axis. The minor amount of twinning observed in longitudinal specimens occurs primarily in these grains. The difference in the rate of twinning in the two types of specimens is clearly evident in Fig. 9, which shows the volume fraction of twins as a function of the total strain for both longitudinal and transverse specimens. These curves show that, for strains below 10 pct, the present zirconium material twins as a function of the strain at a volume fraction rate, which is approximately 20 times higher in the transverse specimens than it is in the longitudinal specimens.

The Contribution of Twinning to the Total Strain

The linearity of the volume fraction twinned curves with respect to the strain (strains less than 10 pct for transverse specimens) is deemed significant. It implies that the twinning deformation is an integral part of the total deformation and, as has been indicated above, it may be the controlling factor in the flow of the transverse specimens.

FIG. 12-9. VOLUME FRACTION OF TWINS AS A FUNCTION OF STRAIN IN PURE ZIRCONIUM TENSILE SPECIMENS DEFORMED AT ROOM TEMPERATURE.

While the nucleation of twins may play a controlling role in the flow of the metal, it is easy to show that even in the transverse specimens, the majority of the deformation is due to slip. Thus, at room temperature, the most important mode of twinning is $\{10\bar{1}2\}$ and, to a first approximation, we may assume that the contribution of twinning to the total deformation is due to this mode alone. The twinning shear for this form of deformation is about 17 pct. The maximum possible contribution which the twinning shear could add to the observed tensile strain is approximately $(1/\sqrt{2})$ times the magnitude of the twinning shear times the volume fraction twinned. However, a more realistic value of the numerical coefficient, taking into account the angular spread of the twins in space and other factors, may be about $(1/2)$. On this basis, we may assume that the total contribution to the tensile strain by the twinning shear is about 0.09 times the volume fraction twinned. According to Fig. 9, the volume fraction twinned at room temperature is about 1.7 times the total strain in transverse specimens (strains less than 10 pct). This means that the contribution of the twinning shear to the total deformation is about 15 pct. It is apparent that even in transverse specimens nearly all of the deformation (85 pct) must occur by slip.

Cooperative Twinning

An interesting twinning phenomenon is visible in Fig. 10. This photograph shows a chain of six connected twins. Each twin in this array passes completely across its own grain and, at a grain boundary, is in nearly perfect alignment with a twin in the neighboring grain on the opposite side of the boundary. Groups of connected twins, like that shown in Fig. 10, have been observed with as many as 15 twins in the chain. This cooperative twinning phenomenon is observed when groups of adjoining grains have nearly the same orientation. When this occurs, it is possible to have sufficiently close alignment of the twinning planes in adjoining grains so as to result in the observed twin chains. The evidence is good that these chains of twins grow by the repeated nucleation of twins in the grains lying ahead of the ends of the chain.

The twin chains visible in Fig. 10 are another strong indication of the cooperative nature of the total deformation in polycrystalline zirconium. In this case, the twinning shear is passed along from grain to grain by the nucleation of another twin. When a twin ends at a grain boundary and no other twin forms in the grain ahead of it, the twinning shear must be assumed to be transferred into the next grain by slip. This transferral of the strain may, however, occur not by simple glide, but rather by the formation of bend planes or kinks which are equivalent to deformation bands.

Twinning in Specimens Deformed at 77°K.

It is interesting to compare the twinning phenomena observed in specimens deformed at 77°K with that found in comparable room temperature specimens. Both longitudinal and transverse specimens show a greater incidence of twinning at the temperature of liquid nitrogen than they do at room temperature. The volume fraction which twins in a longitudinal specimen is still small, however, showing that slip is still the preferred mode of deformation in grains whose basal planes are aligned parallel to the tensile stress axis.

Twinning in specimens deformed at the temperature of liquid nitrogen is much more complicated than it is in specimens deformed at ambient temperatures. At room temperature the primary mode of twinning is $\{10\bar{1}2\}$. Twinning deformation at 77°K involves a much greater incidence of the $\{11\bar{2}1\}$ mode than is observed at room temperature, so that both $\{11\bar{2}1\}$ and $\{10\bar{1}2\}$ are important deformation modes. This signifies that a greater number of twinning modes can operate in any given grain. The extremely complex deformation which results is clearly shown in Fig. 11 which represents the microstructure of a transverse specimen deformed to a strain of 22 pct at 77°K. This photograph should be compared with that of Fig. 5 showing the deformed structure obtained in a transverse specimen strained at room temperature.

Another characteristic of specimens deformed at liquid nitrogen temperatures is the strong tendency for second order

FIG. 12-10. CO-OPERATIVE TWINNING IN A PURE ZIRCONIUM TENSILE SPECIMEN. STRAIN 1.7 PCT. AT A STRAIN RATE $1.6 \times 10^{-2} \text{ MIN}^{-1}$. 300X

FIG. 12-11. THE COMPLEXITY OF THE TWINNING PHENOMENA AT 77° K IS ILLUSTRATED BY THIS PHOTOMICROGRAPH OF A TRANSVERSE TENSILE SPECIMEN DEFORMED TO 29 PCT. STRAIN. 300X

twinning, or the formation of twins inside twins, to occur at this temperature. A well-defined example of second order twinning in a grain of a longitudinal specimen deformed at 77°K is shown in Fig. 12.

The combination of second order twinning with a high multiplicity of possible twinning modes accounts for the extreme complexity of the deformation visible in Fig. 11. Of special significance is the fact that this complex deformation is associated with an increase in ductility of the metal. This is verified by the curves in Fig. 8. Note that the elongation of the 77°K longitudinal specimen is comparable to that of the two specimens tested at room temperature, while that of the transverse 77°K specimen is about one-third greater. This is good evidence that twinning is not an embrittling phenomena per se. The highly complex twinned structure visible in Fig. 11 is associated with an increase in ductility, not a decrease.

FIG. 12-12. SECOND ORDER TWINNING IN A LONGITUDINAL PURE ZIRCONIUM SPECIMEN. PRIMARY TWINS ARE $\{10\bar{1}2\}$.

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A PRELIMINARY EXAMINATION OF THE FORMATION AND UTILIZATION
OF TEXTURE AND ANISOTROPY IN ZIRCALLOY-2

by

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ABSTRACT

The anisotropy of mechanical properties in Zircaloy-2 due to preferred orientation developed during manufacture has caused many difficulties in the fabrication and utilization of mill products. While many have become more aware of the problems and the promises of anisotropy in manufacturing and engineering applications, little effort has been spent in examination, analysis, or control of the development of preferred orientation in Zircaloy-2. The promise of an appreciable increase in permissible design stresses in structures made of this material requires that a thorough study be made of the problem. This paper presents a preliminary examination of the development and utilization of texture preparatory to an experimental study of anisotropy in Zircaloy-2 tubing.

The development of preferred orientation during manufacture of Zircaloy-2 plate, strip, and tubing is qualitatively analyzed in terms of the plastic strain undergone, the modes of deformation operative, the existing anisotropy of flow strengths, and the effects of forming forces of the rolls or dies. The problem of forming structural shapes from anisotropic mill products is discussed and the utilization of the anisotropy of mechanical properties to ease manufacture and to strengthen structures is considered.

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INTRODUCTION

The importance of the anisotropy of mechanical properties of sheet metal during forming of structural shapes has been recognized as a major problem for many years. By empirical methods and research on preferred orientation, the more immediate problems in the control of texture in cubic metals during fabrication have been solved. In some cases, preferred orientation has been sought deliberately to take advantage of the anisotropy of some property, such as the high magnetic permeability of the silicon-iron transformer sheet when the $\langle 001 \rangle$ direction is oriented in the rolling direction. Similar, but frequently much more severe, problems are encountered in all phases of the manufacture and utilization of products of the close-packed-hexagonal metals such as beryllium, magnesium, titanium, and zirconium. This has not been adequately realized. Indeed, it has not been recognized that the mildest anisotropy of mechanical properties obtainable in these materials is much more severe than the maximum anisotropy that can be produced in cubic metals. Further, few designers have been aware that the very great anisotropy of yield strengths present in these materials when highly textured can either seriously limit their use or can be of considerable advantage in strengthening parts and structures.

It is the purpose of this paper to qualitatively analyze the effects of anisotropy of mechanical properties of Zircaloy-2 upon the fabrication of plate, sheet, and tubing, and upon the forming of parts and structural shapes from them. Several advantageous applications of anisotropy will be presented and discussed. Finally, the approach of a current research program to the analysis, prediction, production, and control of texture and to the influence of texture on the strain behavior in Zircaloy-2 tubing will be presented.

The Anisotropy of Mechanical Properties in Plate and Sheet

In a recent study¹ of the effect of fabrication variables on the preferred orientation and anisotropy of mechanical properties in Zircaloy-2 plate it was found that the yield strengths varied, in highly textured polycrystalline material, from a minimum of 52,000 psi to a maximum of 71,000 psi in tension and from 63,000 to 122,000 psi in compression, as shown in Table 1. Further, it was found that the yield strength was 70,000 psi in tension and 101,300 psi in compression for the transverse direction specimens of one lot of material (sched J in Table 1). The proportional limits were found to vary correspondingly. The tensile and compressive stress-strain curves for two of the twenty materials studied are presented in Fig. 1. Also presented are polar plots of the variation of mechanical properties with specimen orientation in the plane of the sheet for these two materials. Such anisotropy of mechanical properties must be considered in the fabrication of mill products, in the forming of shapes, and in the design of structures.

This study has shown that the textures and resulting anisotropy can be modified by control of the fabrication variables, and especially by intermediate beta heat treatments. It has also shown that the three-dimensional anisotropy in plate material may be determined from an analysis of two fractured round tensile specimens. (This measurement allows the purchaser to set specifications of anisotropy and gives the manufacturer a method of quality control.) The change in shape from the original round cross section to a very elliptical one at the fracture is shown in Fig. 2 for a typical longitudinal tensile specimen cut from sched-8 material of Table 1. Both polished ends at the fracture are shown with one rotated 90° relative

Table 1. Anisotropy of Mechanical Properties in Two Lots of Zircaloy-2 Plate

Schedule ^a	Specimen Orientation ^b	0.2% Yield Strength		Ultimate Strength	Elongation % in 1 in.	R.A. ^e	Strain Ratio ^f
		Compression 10 ³ psi ^c	Tension ^d 10 ³ psi	Tension 10 ³ psi			
8	RD	66.7	54.9	67.8	24.2	46.8	0.13
	22 1/2 deg		53.7	66.5	22.5	51.1	0.13
	45 deg		56.2	66.6	25.0	48.8	0.13
	67 1/2 deg		55.8	65.3	25.0	50.1	0.13
	TD	62.7	58.3	68.0	19.5	43.6	0.13
	ND	122.0					
J	RD	65.6	52.0	74.9	22.0	33.6	2.29
	22 1/2 deg		63.2	75.8	18.5	36.2	0.55
	45 deg		66.1	74.3	18.0	41.5	0.81
	67 1/2 deg		71.0	76.6	18.7	44.0	0.59
	TD	101.3	70.0	78.1	21.5	44.8	0.67
	ND	72.5					

^aSchedule 8 - alpha worked (1475 to 1000°F) from forged plate; Schedule J - rolled from 1850°F, 12-in.-diam ingot to 3/4 in. plate with reheat, rolled to 7/16 in. from 1450°F, heated to 1832°F 30 min, water spray quenched, rolled to 5/16 in. at 1000°F, ingot axis in transverse direction. Both materials annealed 30 min at 1450°F.

^bAngle of specimen axis relative to rolling direction. RD = rolling direction; TD = transverse direction; ND = normal direction.

^cCompression test specimen - 0.160 in. diam × 0.160 in. long. S. H. Bush, Compression Testing of Zircaloy-2, HAPD, personal communication (1961).

^dTensile test specimen - 0.125 in. diam × 1 in. gage section, duplicate specimens.

^eR. A. = reduction of area calculated from area of fracture ellipse.

^fRatio of natural contractile strain in normal direction to the natural contractile strain in the plane of the plate. For truly isotropic material, the strain ratio = 1.0 for all specimen orientations.

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FIG. 13-1a. TENSILE AND COMPRESSIVE TRUE STRESS-TRUE STRAIN CURVES FOR SCHED 8 ZIRCALOY-2

FIG. 13-1b. TENSILE AND COMPRESSIVE TRUE STRESS-TRUE STRAIN CURVES FOR SCHED J ZIRCALOY-2

FIG. 13-1c. TENSILE PROPERTIES OF SCHED 8 ZIRCALOY-2 AS A FUNCTION OF TENSILE AXIS IN THE PLANE OF THE PLATE.

FIG. 13-1d TENSILE PROPERTIES OF SCHED J ZIRCALOY-2 AS A FUNCTION OF TENSILE AXIS IN THE PLANE OF THE PLATE.

FIG. 13-2. PHOTOGRAPH OF THE ELLIPTICITY OF CROSS SECTION DEVELOPED IN SCHED 8 ZIRCALOY-2 ROUND TENSILE SPECIMEN. ONE END IS ROTATED 90° TO SHOW THAT THE ELLIPTICITY IS NOT PHOTOGRAPHIC DISTORTION.

to the other, to show that the ellipticity is not photographic distortion. Wherever plastic flow had occurred in this specimen, the shape had changed from round to elliptical. The ratio of plastic strain in the cross section was 0.13 for the normal-to-transverse directions for all values of axial plastic strain. The compression yield strengths for these two directions (Table 1) were 62,700 and 122,000 psi, respectively, while the tensile yield strength in the rolling direction was 54,900 psi. Most of the sheet and strip Zircaloy-2 produced today have essentially these properties. It is hardly surprising that many problems arise in the fabrication of mill products and in the forming of shapes from them. Changing the working temperature will not help appreciably (except to increase the ductility) since, from tensile test data,^{1,2} it has been shown that the strain anisotropy is essentially constant from -190 to 540°C for a given lot of Zircaloy-2.

Deformation Systems in Zircaloy-2

The deformation systems operating in Zircaloy-2 have not been reported but have generally been assumed to be those reported for zirconium^{3,4} (see Fig. 3). No evidence to the contrary has been reported and experiments by Reed-Hill⁵ have tentatively confirmed them to be the same. These systems are $(10\bar{1}0)[\bar{1}2\bar{1}0]$ slip, $\{10\bar{1}2\}$ and $\{11\bar{2}1\}$ twinning in tension along the basal pole, and $\{11\bar{2}2\}$ twinning in compression along the basal pole. The $\{11\bar{2}3\}$ twinning mode for tension along the basal pole has been reported⁴ also but the data are neither conclusive nor complete. It is possible that other twin systems may operate when there is sufficient restraint in one of the principal stress directions.

FIG. 13-3. DEFORMATION SYSTEMS AND CRYSTALLOGRAPHIC PLANES AND DIRECTIONS IN ZIRCONIUM.

An examination of these deformation systems shows that in simple tension along the basal pole, the first plastic flow occurs by $\{10\bar{1}2\}$ twinning. The twinned material is then so oriented relative to the stress axis that it can flow readily by slip. Work-hardening apparently occurs rapidly enough to prevent confinement of the strain to the twinned material, forcing more material to twin. When there is compression along the basal pole, all of the deformation takes place by twinning, through a complicated sequence involving $\{11\bar{2}2\}$, $\{10\bar{1}2\}$, and $\{11\bar{2}1\}$ twinning, until a stable texture is reached. In this stable texture (stable to continued flow in the original compression direction), the basal poles are concentrated in a $\pm 40^\circ$ spread about the compression axis. Once this texture is established, all further deformation takes place by $\{11\bar{2}2\}$ and $\{11\bar{2}1\}$ twinning. While the $\{11\bar{2}1\}$ twin system operates for tension along the basal pole, it can produce thinning of the specimen whenever the basal pole of the particular grain or segment being considered is more than about 18° away from the compression axis. The exact sequence of twinning operations required to produce and keep the stable texture has not yet been worked out. Such a sequence must exist since experiment demonstrates that the final texture is stable to continued deformation. Little, if any, of the required deformation can have occurred by slip (after the stable texture is reached) because none of the twinning modes that can produce the required strains simultaneously orients both the slip plane normal and the slip direction in the plane of strain. If the plastic flow is confined to plane strain and the basal pole is oriented in the direction of the normal to the plane of strain, all of the deformation will take place by slip.

Textures Produced by Fabrication

Conventional mill practice in the production of plate, sheet, and strip Zircaloy-2 involves major reductions at temperatures where the alpha phase is stable. Intermediate and final annealing is usually performed in the range of 1200 to 1550°F, depending on the grain size desired. The material may or may not be given a finishing cold reduction of 10 to 15%. The worked texture produced¹ is that of $[10\bar{1}0] \parallel \text{RD}$, $[11\bar{2}0] \parallel \text{TD}$, and $[0001] \parallel \text{ND}$ or within a 30 to 40° transverse spread about the normal direction. The intensity of the texture in the rolling and transverse directions is moderately strong; that about the normal direction is quite strong. Alpha annealing sharpens the texture and rotates it approximately 30° about the basal pole, usually putting $[11\bar{2}0] \parallel \text{RD}$ and $[10\bar{1}0] \parallel \text{TD}$.

The textures found in tubing vary considerably, seemingly according to the exact details of the sequence of fabrication steps and the fabrication methods. They do have one common feature, a complete absence of basal poles in the axial or longitudinal direction. In various lots of tubing,⁶⁻⁹ the basal pole concentrations have been found to be (1) in the radial direction, (2) in the tangential direction, (3) at 30 to 40° to the radial direction, (4) in both the radial and tangential directions, and (5) randomly distributed between the radial and tangential directions. The methods of manufacture have been (1) drawing with plug or mandrel, (2) tube sinking, (3) swaging, and (4) tube reducing. All the manufacturers started with extruded tubes, but the extrusion ratio varied. The texture found in extruded tubing is apparently influenced by the extrusion ratio in a manner which cannot yet be understood, in part, because the processing variables have not been reported in

sufficient detail. The texture of the finished product has been reported for tubing made by the several processes but the manufacturing steps have not been given in sufficient detail to permit an analytical examination or correlation. Such an examination requires knowledge of die angles, amount of sinking before plug or mandrel is encountered, whether the drawing operation is performed with plug or mandrel or with neither, reductions at each operation, lubrication conditions, etc. Without such data, it appears impossible to analyze the development of the textures reported in the literature.

The formation of texture during mill fabrication can be interpreted, in a simple manner, by examining the changes in texture accompanying plastic flow in a sheet-tensile specimen. Three situations are diagrammed in Fig. 4. The texture of the material represented in Fig. 4a is typical of that produced by conventional rolling mill practice; a strong texture consisting of basal poles ($\langle 0001 \rangle$ directions in the hexagonal cell) normal to the rolling plane. In the necked region of the sheet specimen, it is found that the thickness of the specimen has decreased very little but that the width of the specimen has decreased quite appreciably. In this region the basal poles are still in the original alignment but the "cell" may have been rotated to put a different prism direction in the direction of plastic flow. The strains that have occurred are tensile along the axis of the specimen, compressive in the width direction, and essentially zero in the thickness direction. The specimen will fail by narrowing in the width direction even for a specimen having a width-to-thickness ratio of 8 to 1. By contrast, a sheet-type specimen made of an isotropic material will fail by localized thinning along two lines approximately 55° to the stress axis.¹⁰ The behavior of these Zircaloy-2 specimens can be partially understood by an examination of the yield

FIG. 13-4. TEXTURE CELLS AND STRAIN PATTERNS IN SHEET
TENSILE SPECIMENS OF ZIRCALOY-2

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strengths in compression presented in Table 1, noting that the sched 8 material has the texture under consideration. The compressive yield strength in the normal (thickness) direction (122,000 psi) is twice that in the transverse (width) direction (62,700 psi). The compressive stress-strain curves presented in Fig. 1a show that the work hardening produced by the strain in the width direction will never cause the flow strength to increase to the point that appreciable flow will occur in the thickness direction. The plastic flow occurs entirely by slip. Flow in the thickness direction would have to occur by $\{11\bar{2}2\}$ twinning requiring (from the compressive yield data) nearly twice the stress as flow in the width direction. If one interprets the tensile properties (Fig. 1c) conventionally, this material would be called "isotropic" since the mechanical properties in all directions in the plane of the sheet are essentially the same. Yet, few modern structural materials can be more truly anisotropic. This anisotropy can, however, be quite useful in many applications if it is considered as part of the design problem.

Figures 4b and 4c represent the textures encountered in longitudinal and transverse direction tensile specimens for the sched J material of Table 1. The longitudinal direction specimen will fail by thinning in the thickness direction and will have a large value of "uniform elongation"; but the fracture will be perpendicular to the tensile stress axis, rather than at 55° to it as for an isotropic material. The texture will not change during straining. The transverse direction specimen (Fig. 4c) will fail much like the specimen of Fig. 4a but, prior to fracture, it will experience appreciable flow in the thickness direction. In this case, the basal pole is parallel to the direction of tensile strain with the result that the strain can occur only by $\{10\bar{1}2\}$ twinning. The twinned material becomes favorably oriented for

slip to occur and the specimen lengthens along the tensile axis and thins in the thickness and width directions. It is probable that some of the twinned material will have basal poles aligned in the width direction as well as in the thickness direction. Either alignment will produce the required strains and both of the resulting orientations are stable under further straining. It is difficult to say what the texture in the fracture area will be, since highly localized heterogeneous strain can occur in this region.

Thus, the initial texture will be:

1. Stable if there is compression along the basal pole.
 2. Stable if there is a state of plane strain such that the strain can be accomplished by slip and the basal pole is normal to the plane of strain.
 3. Unstable if the strain is produced by tension along the basal pole, in which case twinning and rotation to one of the above conditions will occur.
- If, then, the directions of strain can be defined in the region of plastic flow, the stability of the entering texture (that just before the deforming process) can be stated and the emerging texture (that just after the deforming process) can be predicted.

The examination of the plastic behavior of the sheet-type tensile specimens (Fig. 4) also allows the prediction of the plastic behavior and load carrying capacity of fabricated shapes having various textures. This, in turn, will permit the selection of the sequence of fabrication operations that uses the anisotropy of the material to maximum advantage during fabrication and yet produces the desired final texture. Finally, an approach such as this is a start toward accurate use of anisotropy in the design of structural members.

Consider the production of plate, sheet, and strip by warm or cold rolling. The forming operation is essentially that of forcing compressive strain to occur in the thickness direction of the material as shown in Fig. 5a. There will also be a tensile strain in the rolling direction, and a small tensile strain in the transverse direction which can, for present purposes, be neglected. If the starting texture is completely random but a major reduction in thickness is required, all grains that are oriented with basal poles near the normal direction will maintain their alignment (within 30 to 40° about the normal) since compressive strain by twinning does not produce a rotation of texture. All grains with basal poles oriented near the rolling direction will undergo tensile strain by $\{10\bar{1}2\}$ twinning and the twinned material will have its basal poles near the normal or transverse direction. All grains having basal poles oriented near the transverse direction will be stable in their orientation unless transverse tensile strain occurs, either generally or locally due to heterogeneous deformation. If transverse tensile strain does occur, it will be by $\{10\bar{1}2\}$ twinning and the twinned material will have its basal poles in the normal or rolling direction. The latter will again be deformed by twinning to finally align the basal pole in the normal direction. Thus, after a sufficient amount of reduction in thickness, almost all grains will have their basal poles oriented near the normal direction of the sheet. It has generally been found that the texture which is stable during extensive plastic flow is that which allows duplex deformation. This requirement can be fulfilled only if the basal poles are oriented approximately 30 to 40° each side of the sheet normal and a $\langle 10\bar{1}0 \rangle$ direction is near the rolling direction. This texture also requires that all of the plastic flow takes place by twinning, none by slip. Anyone who has heard annealed Zircaloy-2 cold rolled will not doubt that this is the case.

FIG. 13-5. STRAIN STATES DURING FABRICATION OF ZIRCALLOY-2.

A similar situation exists in the manufacture of tubing by plug and mandrel drawing, as shown schematically in Fig. 5b. The strain conditions are shown for two textures, one having basal poles oriented in the radial direction and the other having basal poles in the tangential direction. The tubing undergoes simultaneous tensile strain in the axial direction, compressive strain in the circumferential direction, and either no change in wall thickness (plane strain) or wall thinning by compressive strain in the radial direction. The texture with basal poles in the radial direction (± 30 to 40°) will be stable throughout the deformation. Any other texture will reorient to this texture, with the exception of those grains with basal poles in the tangential direction. Such grains will not reorient unless there is localized heterogeneous deformation. Thus, if the entering texture is random, the final texture will be strongly oriented with the basal poles aligned within ± 30 to 40° of the radial direction. It does, however, seem possible that the texture could be caused to vary from basal poles in the radial direction to basal poles in the tangential direction by varying the reduction in circumference relative to the reduction in thickness in each drawing pass. Since specific compressive loads will vary with die angles, total reductions per pass, and frictional forces on the die, plug, and mandrel surfaces, the strain pattern actually existing in the flowing material is not known. Consequently, the prediction of the emerging texture cannot be exact.

The plastic flow occurring in the operation called tube sinking is somewhat different from that of plug and mandrel drawing if wall thickening occurs, since this will produce tensile strain in the radial direction. The conditions are shown in Fig. 5c. If the entering texture consists of basal poles oriented in the radial direction, some of the material will undergo

twinning in tension and the basal poles of the twins will be oriented in the tangential direction. The remainder of the grains will maintain their orientation. The amount of material reoriented will depend on the amount of wall thickening that occurs. If, however, the texture of the entering material consists of basal poles in the tangential direction, the texture will not change, since this orientation is stable under compressive strain in the direction of the basal pole (circumferential contraction is by compression in the tangential direction).

In tube reducing, material is forced to flow (Fig. 5d) by the action of tapered grooves in an oscillating roll and a tapered mandrel which moves with the rolls. A given element in the tube is simultaneously compressed radially between the rolls and the mandrel and tangentially by the tapered grooves of the rolls. Axial elongation results, but there is no externally applied tensile load as in drawing. If the entering texture consists of basal poles oriented in either the radial or the tangential direction or both, the texture will be stable, as diagrammed in Fig. 5d. If, however, sinking is allowed before the mandrel is encountered (wall thickening), some of the basal poles in the radial direction will be moved to the tangential direction by tensile twinning, and the final texture will be a mixture, basal poles being concentrated in both the radial and tangential directions. If the entering material is randomly oriented, only those grains having basal poles oriented near the axial direction will be displaced from that direction by twinning. Thus, the emerging texture for a randomly oriented entering material should be one with an absence of basal poles in the axial direction and with the basal poles randomly distributed between the radial and the tangential directions.

A similar situation exists for tubing fabricated by swaging on a mandrel, with the exception that a sinking operation definitely occurs in the first part of the swaging die. In swaging, the emerging material will show an absence of basal poles in the axial direction if no major reduction occurs after the mandrel is contacted. If there is a major reduction in thickness after the mandrel is contacted, most of the strain will be confined to the radial direction and the texture will consist of basal poles oriented in the radial direction (± 30 to 40°).

Again, it seems possible that the intensity and orientation of the emerging texture can be altered by varying the relative amounts of circumferential and radial strains in these operations.

The Influence of Texture on Forces During Fabrication

The extreme anisotropy in yield and flow strengths can cause appreciable difficulty during fabrication. On the other hand, if recognized and properly used, it can greatly reduce the working forces required in the operation.

Rolling is primarily compression (plane strain), there being compressive flow in the thickness direction, tensile flow in the rolling direction, and little if any flow in the transverse direction (for conditions where the width is many times the thickness). The texture usually produced in Zircaloy-2 consists of basal poles within $\pm 40^\circ$ of the normal to the rolling plane. Since the compressive flow strength for this texture is high, the roll forces will be high. Reduction of roll forces can be accomplished by warm or hot rolling, tension rolling with high fore and back tension, or frequent annealing.

In plug drawing and in sinking, the drawing force is applied axially to the material that has emerged from the die. The most desirable texture, from

the standpoint of working forces, in the material both entering and leaving the die consists of basal poles in the radial direction. This texture, however, is the one most likely to cause surface cracking at the point where the tubing leaves the die, a region of high tensile stress concentration. Material with this texture has maximum strength under axial tension (produced by the applied drawing load) since there is restraint in the circumferential direction and axial tensile strain can be produced only if accompanied by wall thinning by compression $\{11\bar{2}2\}$ twinning. The texture having basal poles in the tangential direction will be weakest in such axial tension because wall thinning can occur by slip. Since the forces required to strain the material in the die should be nearly the same for a given geometry of die and plug or mandrel, material having the first texture may be drawn under conditions where material with the second cannot, simply because they sustain different axial loads before failure.

The forming forces required in tube reducing should be almost independent of the entering texture, since all of the applied forces are compressive and should depend almost entirely on the reductions in wall thickness and circumference. They will, however, be relatively high since little of the flow can be by slip. The load-bearing ability of the emerging texture is unimportant here, since there is no externally applied axial load.

Applications of Texture Control in Forming Operations

One may easily demonstrate the importance of control of texture by varying the texture of the stock for various sheet metal forming operations, such as bending of sheet, drawing of cups, and stretch forming. With certain textures, the material will crack in the bend in forming of boxes, fracture

in the wall of the cup or in the flange of the blank in cup drawing, or wrinkle in stretch forming while none of these happen if the material has certain other textures. Some shapes may be impossible to make unless the stock has exactly the right texture for the operation.

Consider the problem of bending of sheet stock to form sharp corners for making boxes and frames. The forces and strains involved are shown schematically in Fig. 6a. As the stock is bent, the outer surface is placed in tension and the inner surface in compression. The neutral axis is, in general, not located at the center line but is displaced toward the compression surface. Since there is restraint along the bend axis, no transverse strain may occur (except at the sides where, though undesirable, it is usually small). Thus, all of the tensile strain occurring in the outer layer (outside the neutral axis) must be accompanied by radial compressive strain. The "available ductility" of the material limits the amount of bending that can be accommodated. If it is small, the bend radius must be large or the material will crack during bending. Because of restraints (no transverse strain), the center portion will be in biaxial tension, limiting the "available ductility" even more, and cracking will start at this point and progress through the thickness and along the axis of bend.

If the basal poles are in the direction of the bend radius (see Fig. 6a), all of the tensile strain must occur by $\{11\bar{2}2\}$ twinning. This requires very high flow stresses and the texture is stable under this loading. The tensile stress in the surface must be high if the necessary plastic strain is to occur. At room temperature, the ductility under these conditions is limited. Therefore, the piece will crack during bending if the bend radius is small. If material of this texture must be used, the only recourse is to increase the forming temperature or the bend radius.

FIG. 13-6. STRAIN STATES IN SHEET METAL FORMING OF ZIRCALOY-2.

If the texture is such that the basal poles are parallel to the bend direction, the problem is eased to some extent and the bend radius can be reduced without encountering cracking. The initial tensile strain along the basal poles is accomplished by $\{10\bar{1}2\}$ twinning with a decrease in thickness (there being side restraint). The twinned material is now oriented to permit further thinning to occur by compressive $\{11\bar{2}2\}$ twinning (the basal pole will be in the radial direction, not the transverse, because no strain is permitted to take place in the transverse direction). The twinned material is now in the same orientation as the previous texture and will have the same strain state, but appreciable strain has already occurred by the $\{10\bar{1}2\}$ twinning. Thus, the "available ductility" of the starting texture is increased by the amount of strain produced by the $\{10\bar{1}2\}$ twinning.

If the basal poles are parallel to the bend axis, all of the strain, both tensile in the bend direction and compressive in the radial direction, can be accomplished entirely by slip. The bending forces will be low and the "available ductility" will be high. Furthermore, work-hardening will occur rapidly enough to prevent localized necking, and the bend radius can be decreased quite appreciably. The tendency for transverse strain to occur at the edges (which are not in unrestraint) will be resisted by the very high flow stress required for strain by compression along the basal pole. In this case, the strong texture can be an advantage, when compared to isotropic material, if it is important that the edges not deform during the bending operation.

A highly developed texture can be used to considerable advantage in cup drawing if the basal poles are in the normal (thickness) direction of the drawing blank.¹¹ The strain states in the drawing blank and the "cell"

orientations for two textures during the drawing operations are shown schematically in Fig. 6b. The strain state in the flange of the cup is one of tensile strain in the radial direction, compressive strain in the circumferential direction, and tensile strain in the thickness direction if plane strain conditions are not enforced by a hold-down ring. In the wall of the cup, there is tensile strain in the direction of punch movement, compressive strain in the wall thickness direction, and restraint in the circumferential direction (the punch prevents a decrease in the circumference). In the bottom of the cup, the center is in pure biaxial tension, producing tensile strain in the radial direction and compressive strain in the thickness direction.

If the material has basal poles oriented in the thickness direction of the drawing blank, the drawing operation is eased considerably and cups can be drawn much deeper than with an isotropic material.¹¹ In the flange region, the strain is produced entirely by slip and thickening is resisted by the high yield stress required for $\{11\bar{2}2\}$ twinning. In the wall of the cup, tensile fracture is resisted because it requires wall thinning and compressive strains along the basal pole require quite large stresses. In the bottom of the cup, thinning is resisted for the same reason. Thus, flow is easy where it is desirable, as in the flange region, and difficult where it is undesirable, as in the wall and bottom of the cup. Further, the texture is symmetric about the punch axis, decreasing the tendency for "earring."

If the basal poles of the material are aligned in an arbitrary direction in the sheet, the texture will not be symmetric about the punch axis, giving the two different "textures" (relative to the strain axes) shown in Fig. 6b. There will be a point around the punch axis where the basal poles are aligned in the radial direction of the drawing blank. The tensile strain at this

point will occur by $\{10\bar{1}2\}$ twinning. Part of the twinned material will have its basal poles aligned in the thickness direction and will then be stable, further deformation occurring by slip. The other part of the twinned material will have its basal poles aligned in the circumferential direction and would be stable if undisturbed. However, further strain must then occur by $\{11\bar{2}2\}$ twinning and the required stresses will be high, causing heterogeneous strain, since nearby regions can flow by slip. Texture rotation will probably occur until all of the deformed material has the basal poles aligned in the thickness direction. Thus, this portion of the flange will finally have the desirable texture after a sufficient amount of strain has occurred. The surface may be rough, since $\{10\bar{1}2\}$ twinning can also produce localized thinning of the flange.

Now consider the effect of this texture at locations in the flange at 90° to that discussed above. At these locations, the basal poles will be aligned in the circumferential direction and all circumferential strain will have to occur by $\{11\bar{2}2\}$ twinning (compression along the basal pole). As a result, the forces required for such deformation in this part of the flange will be high. It is probable that thinning by slip will occur instead, leading to fracture at or near the throat of the die. In the wall of the cup, wall thinning can occur readily by slip, and the cup is again likely to fracture. In the bottom of the cup, the texture is such that wall thinning can occur by $\{10\bar{1}2\}$ twinning and by slip. Thus, the drawing operation is hampered by this texture at all points in the blank and any pronounced texture having basal poles in the plane of the sheet is quite undesirable.

A similar situation exists in stretch forming. If the material texture consists of basal poles normal to the sheet (see Fig. 6c), it will be desirably symmetric but all strain must be accomplished by $\{11\bar{2}2\}$ twinning and high forces

will be required. If the texture consists of basal poles in some direction in the sheet, the forming forces will be lower but the excessive strain anisotropy may require a rejection of the part. Strain in one direction must be accomplished by $\{10\bar{1}2\}$ twinning (at relatively high stresses) and, at 90° to that direction, the strain will be accomplished by slip. Such a texture will be undesirable if the formed part is hemispherical but it may be desirable if the part is ellipsoidal and the basal pole of the texture is perpendicular to the major axis of the ellipsoid (see Fig. 6d).

Application of Texture Control in Design of Structures

Failure to consider the anisotropy of yield and flow strengths of highly textured Zircaloy-2 can cause serious problems in the design and construction of engineering structures. Alternately, it can be of considerable advantage in increasing permissible design stresses and structural loads if it is used properly. Since any yielding will be considered failure, decreased ductility (if any) is not important. For example, the principal stress operating in internally pressurized vessels is that of hoop tension. Unless the ends of the vessel are fixed, there will be a second tensile stress, orthogonal to the first, also produced by the internal pressure. Such stresses produce biaxial tensile loads in the wall of the vessel, and failure will occur by bulging and thinning of the wall. If the vessel is constructed of highly textured material having the basal poles oriented in the thickness direction, the failure stresses will be considerably higher than for any other texture, including random (which has isotropic properties). For any strain to occur in material having this texture, $\{11\bar{2}2\}$ twinning (compression) must occur. The yield stress in compression for $\{11\bar{2}2\}$ twinning is 122,000 psi. In comparison, the design

value that would normally be used is that of the yield strength of a uniaxial tensile specimen of the sheet material, a value of 55,000 psi for this material (see Table 1, sched 8). Thus, a proper recognition of the role of texture in design problems will permit a design stress more than twice that permitted by conventional design criteria (which were developed for structures built of steel).

A similar situation exists for structural members made of tubing. If the basal poles are strongly oriented in the radial direction in the tubing, the axial tensile load required to cause yielding will be considerably higher than if the basal poles are oriented in the tangential direction or if the texture is random (see Fig. 5c, emerging textures). By similar reasoning, the buckling load or column stiffness should be a maximum if the basal poles are strongly oriented in the radial direction.

If a structural member is made of sheet (or can be considered to be made of sheet, such as I-beams assembled from sheet by welding), the load carrying ability should be greatest when the texture consists of basal poles strongly oriented in the direction of the normal to the plane of the sheet. In all of these uses, the part can yield only if simultaneous thinning occurs. But thinning of this texture requires $\{11\bar{2}2\}$ twinning (compression along the basal pole) and, consequently, very high flow stresses.

Future Research Work

The above analysis of the problems associated with texture and with its development and control has been the result of the previous work performed on rolled plate and sheet Zircaloy-2 and of the preliminary planning for a similar study to be conducted on Zircaloy-2 tubing. A more detailed analysis of the

development of texture during fabrication, of the strain patterns present in the deforming region for different fabrication processes, and of the utilization of texture to advantage during processing and in structural design is presently underway. This analysis is also serving as a guide for setting specifications for the sequence of operations that hopefully will produce the varied textures needed for this tubing study.

The tubing study proposed will determine the effects of various fabrication variables (including intermediate beta heat treatments) on the type of texture produced and the resulting anisotropy of strain and of yield strengths. The anisotropy of flow strengths and of strain under different states of stress will be studied using a technique which is an extension of the methods developed to investigate plastic flow in torsion in rod and tubing.^{1,2} (Unfortunately for our purposes, the authors of these earlier studies discarded the data for those specimens which proved to be anisotropic.) The testing device is presently being designed to read photographically the distortion of a grid of squares (placed on the specimen by photoetching and then anodizing) while the specimen is being stressed by any selected combination of internal pressure, axial loading, and torsional loading. The internal volume will be continuously measured. Intermittent readings during each test will be retained for computer analysis together with the instantaneous axial and torsional strains and the appropriate loads. From the computer analysis, the stress-strain curves for the average grid square, the squares of maximum and minimum strains, and the changes in wall thickness for specific grid squares or the average change for the grid can be obtained as functions of the load variables.

As the determination of the preferred orientation in each test specimen is of prime importance in the tubing study, a new method of determining the preferred orientation (at least for the intensity and orientation of the basal pole) is being developed. This method utilizes the anisotropy of metallographically prepared specimens in polarized light. The intensity of reflected polarized light at angles of rotation relative to selected fabrication directions is measured photoelectrically on a microscope. Preliminary studies using manual rotation and visual reading of the indicating meter have been quite promising but are somewhat tedious and slow. Quantitative analysis of the curves of intensity versus angle of rotation has been unwarranted because proper standards of light intensity, alignment of the plane of polarization in the microscope, and specimen preparation have not been adequately determined. The measuring technique is being automated to plot the intensity versus angle of rotation directly on an x-y recorder and studies are being conducted to determine the standards required. If the method proves successful, and there are indications that it will, the time and effort required to determine the principal components of the texture and their intensity will be decreased considerably from that necessary for x-ray diffraction analysis. In addition, it appears quite feasible to determine textures in thin wall tubing from inner to outer surfaces without the very tedious preparation of specimens required for x-ray diffraction techniques. The rapidity and ease of the method makes practical a rather extensive study of the variation of texture from front end to back end of tubing at various stages of processing.

The proposed study of anisotropy in tubing is only a part of the research program on zirconium alloys in the Zirconium Metallurgy Group at ORNL. Studies presently underway are (1) a basic study of the optical properties of oxide

Films in situ on zirconium alloy specimens in an attempt to determine the defect structure and defect concentration in the oxide as functions of alloying element, oxidizing environment, film thickness, and crystallographic orientation; (2) determination of the oxidation-corrosion rates, by new and more sensitive techniques, as affected by the above variables; (3) methods of production of large single crystals of various alpha-zirconium alloys for the above studies and for basic studies of deformation mechanisms; (4) the correct phase boundaries in the zirconium-rich end of the zirconium-niobium phase diagram; and (5) determination of the transformation kinetics, mechanisms, and morphologies for a wide range of zirconium-base alloy systems.

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Much of the above analyses of texture production and influence was stimulated by a paper presented at the Ninth Sagamore Conference "Deformation Processing" August, 1962, Sagamore, New York. The paper was "Strength and Plasticity of Textured Metals" by W. F. Hosford, Jr., and W. A. Backofen, Metals Processing Laboratory, Massachusetts Institute of Technology.

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TENSILE PROPERTIES OF ZIRCALLOY
WITH ORIENTED HYDRIDES

by

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ABSTRACT

Room temperature tensile tests were conducted to determine the effect of hydrogen content and hydride orientation on the tensile properties of Zircaloy-4 tubing. It was found that hydride platelets oriented nearly perpendicular to the deforming tensile stress caused large reductions in strength and ductility, whereas the platelets oriented nearly parallel to deforming stress had little effect on the tensile properties. All specimens containing more than 50 ppm hydrogen as "normal" (perpendicular) hydrides exhibited no macroscopic ductility, irrespective of the total hydrogen content.

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TENSILE PROPERTIES OF ZIRCALOY WITH ORIENTED HYDRIDES*

INTRODUCTION

Early failures of Zircaloy-clad oxide fuel tubes irradiated at Savannah River Plant were attributed to adverse hydriding of Zircaloy cladding.⁽¹⁾ The brittle cladding failures occurred in hydrided regions that contained 500 to 800 ppm hydrogen precipitated radially as zirconium hydride. Although the effect of hydrogen on the mechanical properties of Zircaloy has been investigated,^(2,3) the results of those tests indicate that annealed Zircaloy-2 containing 1000 ppm H₂ should have ductility values in excess of 10% total elongation and 12% reduction in area. These values were in contrast to the 0.5% elongation and <0.1% reduction in area observed in the fractured cladding of the oxide fuel tube. We believe that in Burton's⁽²⁾ specimens the hydride platelets were oriented parallel to the stress axis, while in the cladding of the failed oxide fuel tubes the hydrides were known to be oriented perpendicular to the stress axis. This comparison suggests that the influence of hydrogen on the mechanical properties was determined by the orientation of the hydride platelets. Since this variable was not considered in the previous investigations, the results of those studies may have been biased by favorable hydride orientations. Therefore, experiments were begun at SRL to determine the effects of hydrogen content and hydride

*The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

orientation on the mechanical properties of Zircaloy. The results to date have been extremely interesting in their portent for reactor designers and operators, and are presented in this paper as information since a definition of mechanisms is not complete at this time.

SUMMARY

The tensile properties of the Zircaloy specimens were extremely variable with hydrogen contents under 100 ppm. Analysis of the data indicated that the reductions in strength and ductility were caused by the amount of hydride that was oriented perpendicular to the deforming stress.

DISCUSSION

Experimental Procedure

The specimens used in these tests were machined from extruded-and-drawn Zircaloy-4 tubing, hydrided to a predetermined hydrogen content and then treated to orient the hydrides before tensile testing at room temperature. Circumferential sections of extruded-and-drawn tubing were used because they had been shown to be highly susceptible to stress orientation of hydride platelets, which permitted large variations in hydride orientation to be produced.

Sections of tubing were slit longitudinally, flattened by hand, and then machined to the dimensions shown in Figure 1. Although the flattening operation worked the material to a limited extent, it had little effect on the tensile properties. Specimens flattened by different persons had very similar tensile properties.

FIG. 14-1. DIMENSIONS OF TENSILE SPECIMENS

The tensile specimens were hydrided to the desired hydrogen contents in dry hydrogen at 400°C in a modified Sieverts-type apparatus. Several specimens were also hydrided by pickup of hydrogen during corrosion in a static steam autoclave at 1500 psig and 400°C. The results of the tensile tests were not influenced by the hydriding technique.

Various hydride orientations were produced by the application of stress-orientation techniques. Previous work at SRL had shown that an applied tensile stress during hydride precipitation caused the hydride platelets to tend to orient perpendicular to the stress axis, and that the degree of orientation was a function of the stress level. For stress orientation, the specimens were placed in Baldwin-Hamilton creep machines and solution annealed for 16 to 18 hours at 415°C. While at temperature, the specimens were loaded to the desired stress then cooled slowly to room temperature in 6 hours to precipitate the hydride. The stresses on different test specimens during hydride precipitation varied from 0 to 25,000 psi.

The specimens were tested to fracture on a Baldwin tensile machine. The load-elongation data were recorded by an autographic recorder using a microformer-type extensometer which was operable to fracture. The ultimate tensile strength and 0.2% offset yield strength were determined from the load-elongation curve and pre-test specimen measurements. Total elongations and reductions in area were determined from pre- and post-test measurements.

Orientations of the hydride platelets were determined from a photomicrograph taken away from the area of fracture. The hydride platelets were counted on the photomicrograph

through an overlay grid that contained lines at 45 degrees to the stress axis. The per cent of the precipitated platelets lying within approximately 50 to 90 degrees to the stress axis were reported as "normal" (perpendicular), and varied from 30 to 95% in different specimens.

The tensile properties were compared with total hydrogen content and also with a new parameter termed "effective hydrogen content." Effective hydrogen content is the product of the fraction of hydride precipitates that are "normal" to the deforming stress and the hydrogen content at the fracture, as determined by vacuum extraction, or

$$H_{\text{eff}} = H_t f_N$$

where

H_{eff} = effective hydrogen content

H_t = total hydrogen content

$f_N = \frac{\text{platelets lying at 50 to } 90^\circ \text{ from the stress direction}}{\text{total platelets}}$

Throughout this paper f_N is used as a measure of hydride orientation. For example, in a sample that has been hydrided but not stress oriented $f_N = 0.35$, while in a highly stress-oriented specimen $f_N = 0.90$.

RESULTS

The tensile properties of the hydrided Zircaloy specimens, Table I, were extremely variable with total hydrogen contents, H_t , up to 120 ppm, the limit of these tests. As the H_t increased from the nominal 10 ppm to 50 ppm, the yield and ultimate strengths increased and the reduction in area and

TABLE I

TENSILE AND HYDROGEN DATA FOR ZIRCALOY-4 SPECIMENS

H_t , ppm	f_N	H_{eff} , ppm	Ultimate Tensile Strength, psi	Yield Strength, psi	Elongation, %	Reduction in Area, %
37	0.35	12	89,000	80,000	11.5	39
37	0.55	20	88,000	85,000	12.5	35
37	0.72	27	92,000	87,000	2.5	17
37	0.81	30	87,000	82,000	3.0	12
39	0.78	30	93,000	90,000	(a)	20
36	0.33	12	87,000	83,000	(a)	27
37	0.47	17	93,000	90,000	(a)	20
25	0.69	17	92,000	87,000	5	19
35	0.77	27	90,000	88,000	(a)	5
46	0.91	42	89,000	85,000	2.5	4
38	0.35	13	90,000	87,000	5	28
40	0.73	29	90,000	88,000	3	22
56	0.72	40	93,000	90,000	1	3
63	0.80	50	86,000	85,000	<1	0
68	0.91	62	89,000	88,000	0	0
62	0.34	21	85,000	82,000	5	25
83	0.72	60	68,000	-	<1	0
66	0.68	45	69,000	-	0	0
120	0.85	102	51,000	-	0	0
80	0.96	77	49,000	-	0	0
62	0.29	18	85,000	80,000	3.7	29
118	0.50	59	80,000	-	<1	0
77	0.63	48	82,500	-	<1	0
64	0.85	55	57,000	-	0	0
121	0.89	108	59,000	-	0	0
8	-	2	77,000	61,000	18	44
8	0.29	2	83,000	68,000	16	42
9	0.32	3	80,000	62,000	20	47
11	(b)	3	78,000	68,000	16	42
11	(b)	3	78,000	68,000	18	38
11	(b)	3	77,000	68,000	18	38

(a) Fracture occurred out of gage length.

(b) Estimated at 0.30.

total elongation decreased due to the second-phase hardening effect caused by the $\text{ZrH}_{1.6}$ particles. With H_t above 50 ppm the strength decreased, but the amount of decrease varied widely with the hydride orientation. For example, specimens containing 80 ppm H_t failed at 83,000 psi with $f_N = 0.63$, but at 50,000 psi with $f_N = 0.96$. Above 50 ppm H_t the ductility continued to decrease with increasing H_t but was even more sensitive to hydride orientation than was the strength. Many specimens with $H_t < 100$ ppm but high f_N fractured before any macroscopic deformation was observed; the stress-strain curves for two specimens are shown in Figure 2.

A comparison of the strength and ductility with the total hydrogen is shown in Figures 3 and 4.

Analysis of the tensile and hydride data presented in Figures 3 and 4 indicated that the tensile properties were being controlled by the amount of perpendicularly oriented hydrides, not the total hydrogen content. The relationship appeared to correlate as follows. Parallel hydrides, low f_N , caused second-phase strengthening with correspondingly small decreases in ductility up to high H_t , at least > 500 ppm. There was no evidence of brittle behavior. When the hydrides exhibited no obvious preferred orientation, $f_N \sim 0.4$, the extent of the second-phase strengthening began to be limited by brittle behavior at high $H_t \sim 200$ ppm. As the value of f_N increased, brittle behavior was exhibited at lower H_t . The comparison of the strength and ductility data with H_{eff} is shown in Figures 5 and 6.

A) Stress-strain Curve for Specimen Containing 43 ppm H_2 Oriented so that $f_N = 0.8$

B) Stress-strain Curve for Specimen Containing 80 ppm H_2 Oriented so that $f_N = 0.96$

FIG. 14-2 TYPICAL STRESS-STRAIN CURVES FOR "BRITTLE" FRACTURE

FIG. 14-3. ZIRCALLOY STRENGTH COMPARED TO TOTAL HYDROGEN

FIG. 14-4. ZIRCALLOY DUCTILITY COMPARED TO TOTAL HYDROGEN

FIG. 14-5. ZIRCALOY STRENGTH COMPARED TO EFFECTIVE HYDROGEN

FIG. 14-6. ZIRCALOY DUCTILITY COMPARED TO EFFECTIVE HYDROGEN

A definite, causal relationship is suggested by the correlation of strength and ductility with H_{eff} . The correlation of ductility with H_{eff} is exceptionally good considering the specimen shape (thin sheet) and the possible variation in hydrogen content withing the rather large samples, $3/8 \times 1/2$ inch, that were necessary for H_2 analyses. The variation in strength at constant H_{eff} is larger than the normal scatter of tensile data, but is not excessive considering that the data is subject to the variations listed for ductility as well as the wide variations in strength data normally caused by brittle behavior.

Examination of Figures 5 and 6 shows that completely brittle behavior and unpredictable strengths can be expected at room temperature when the H_{eff} is greater than 50 ppm, regardless of the H_t . It is interesting to note that brittle behavior would be expected at H_t of 1000 ppm with $f_N = 0.05$, but at H_t of 55 ppm with $f_N = 0.95$. These differences emphasize the importance of considering H_{eff} as well as H_t when evaluating and reporting the properties of Zircaloy.

Another factor that contributes to the brittle behavior is the grouping of the hydride platelets in rows, end to end, that occurs on slow cooling. An attempt was made to evaluate this aspect by fast cooling several specimens under stress to produce homogeneously dispersed, oriented platelets; photomicrographs of the two dispersions of the hydrides are shown in Figure 7. The specimens with dispersed platelets exhibited slightly higher strength and ductility than the specimens with the grouped platelets. It should be noted that the platelet dispersion should not affect specimens with parallel platelets.

Specimen Containing Grouped Hydrides

↑100x

Specimen Containing Homogeneously Dispersed Hydrides

FIG. 14-7.

PHOTOMICROGRAPHS SHOWING TWO TYPES OF
HYDRIDE DISPERSION IN ZIRCALOY-4

The effect of platelets near 45 degrees to the stress would be an additional factor causing scatter in the data but was considered negligible in these tests since the fraction of such platelets was usually less than 0.1.

CONCLUSIONS

The room temperature tensile properties of Zircaloy-4 were sensitive to hydride platelet orientation as well as to hydrogen content up to 120 ppm H₂, the limit of testing to date. The following points were established.

1. The effect of hydrogen on the tensile properties was determined by the hydrides that were oriented "normal" to the tensile stress.
2. Effective hydrogen contents of less than 40 ppm H₂ increased the strength and decreased the ductility of the Zircaloy.
3. Effective hydrogen contents greater than 40 ppm H₂ decreased both the strength and ductility of the Zircaloy to the extent that in samples that contained an excess of 50 ppm effective hydrogen, no macroscopic ductility was observed, and fracture occurred at stresses as low as 50,000 psi.

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THE OXIDATION OF ZIRCONIUM BINARY ALLOYS
IN 700°C OXYGEN FOR TIMES UP TO 200 DAYS

by

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THE OXIDATION OF ZIRCONIUM BINARY ALLOYS
IN 700°C OXYGEN FOR TIMES UP TO 200 DAYS*

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INTRODUCTION

The scaling of zirconium and zirconium alloys in oxygen shows two characteristics which have not received a satisfactory explanation. The first is the cubic rate law in which the slope of a log-log plot of weight gain vs. time is close to 0.33. The second is a transition in the rate law from the initial behavior to approximately a linear dependence of weight gain on time. The transition may be accompanied by changes in color and flaking of the oxide. Various experimental conditions appear to be important in determining the occurrence of these phenomena as evidenced by the fact that some investigators^{1,2} have found a parabolic law instead of a cubic law, and sequential transitions have been observed in water vapor.¹²

The origin of the cubic law has been considered by various investigators who have suggested either electron flow from the metal¹³ for relatively thin films or oxygen diffusion into the metal.^{14,15} Sense¹¹ pointed out that the high solubility of oxygen in zirconium is not a sufficient condition to account for a cubic rate law when the value of the diffusion constant in the metal is concentration-independent. It is necessary to assume that the diffusion "constant" is dependent on the oxygen concentration in the metal as first suggested by Kofstad and Hauffe.¹⁴

Another interesting hypothesis was that of Smeltzer¹⁶ who proposed that the cubic law could be understood as a transient behavior prior to establishment of a parabolic law. Smeltzer pointed out that if oxide growth took place by means of both volume diffusion and diffusion along low-resistance paths and the latter process became progressively less important the initial rate law would eventually become parabolic. On the basis of this assumption a semi-empirical equation was derived which fitted selected data for the oxidation of titanium, zirconium and hafnium. It was only necessary to determine the intercept at zero time and the slope of the data on a parabolic plot. According to this analysis a cubic slope will ultimately change to parabolic.

In the study by Porte, Schnitzlein, Vogel and Fischer⁹ of the oxidation of zirconium and zirconium binary alloys the oxidation rate law and time to transition were found to change over wide limits depending upon the alloying additive. Approximately half of the alloys studied by Porte did not show transition within the time interval of 1400 minutes. Consequently, this

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arbitrary time restriction left certain questions unanswered, such as the relationship between the initial rates and the transition times and the relationship between unalloyed zirconium and the alloys which had not shown transition. Three alloying additives lowered the cubic oxidation rate as compared to unalloyed zirconium, and it was possible that these would also show longer times to transition.

EXPERIMENTAL

A direct extension of Porte's study was possible because samples of all the alloys of interest were still available as well as the original data. The experimental conditions were 700°C in oxygen at 1 atm. pressure. Atmospheric pressure was used for convenience because Porte had showed that the oxidation rate was insensitive to pressure in the range of 50 to 800 torr.

The alloys which were studied are listed in Table I together with the data obtained in the study by Porte. Most of these binary alloys had showed no transition in the nominal composition ranges of 1, 2 and 4 atom per cent. (Analyzed compositions are given in the table.) These alloys contained: Be, Co, Cr, Cu, Fe, Hf, Ni and W. In this set of alloys it was decided not to devote further study to the intermediate 2 a/o compositions. Tungsten was an exception because a 4 a/o W alloy had not been prepared originally. The remaining alloys (containing C, Mo, Si, Pt or U) had showed transition in the higher composition ranges (4 a/o for uranium and 2 a/o in the case of the others). It was thought that these would show transition sooner than the first set of alloys, and this expectation was proven correct.

If a detailed comparison is made between Table I and the original data presented by Porte some minor differences will be found in the slope of the log-log plot (6 cases) and in most of the weight gains at the end of the runs. The reason for this is that Porte presented an average of several curves, and a single curve was selected for purposes of comparing with the long-term data. The figures given are those for the single curve. In every case except 2 a/o W the differences from Porte's averages were negligible.

Complete analyses of these materials are found in the original study. They were typical for zirconium alloys and need not be reproduced. The alloys were believed to be in the as-cast condition, but information on this point was lacking. Metallographic examination was undertaken and indicated as-cast structures with several exceptions where evidence of working was found. The alloys which should have had the cleanest microstructure, e.g. the hafnium alloy, contained second phase constituents which seemed to contradict the analyses.

Specimens were cut into small parallelepipeds approximately 0.65 cm square and 0.34 cm thick. They were wet ground to 400 grit silicon carbide and finished by dry grinding with 600 grit paper in order to duplicate the final surface treatment used by Porte. The specimens were wrapped in plati-

TABLE I

Oxidation of Zirconium Alloys Which Followed the Cubic Rate Law
With No Transition Up to 1400 Minutes. (700°C and 200 mm Oxygen)

Alloy Composition Atomic and Weight Per Cents			Cubic Rate Constant $[10^4(\text{mg}/\text{dm}^2)^3 \text{ min}^{-1}]$	Length of Run (Min.)	Weight Gain (mg/dm^2)	Color and Character of Oxide Film
Unalloyed Zr.			1.6	1300	260	Blue-gray; adherent
<u>a/o</u>		<u>w/o</u>				
0.90	Be	0.09	1.2	1400	250	Blue (gold tinge); adherent
4.23	Be	0.44	1.1	1400	240	Black with white raised edges; adherent
0.65	C	0.086	2.5	1400	330	Silver-gold with white edges and spots; adherent
0.86	Co	0.55	1.6	1285	270	Gray-black; adherent
3.72	Co	2.44	2.2	1150	285	Gray (gold tinge); adherent
0.77	Cr	0.44	1.7	1400	270	Black; adherent
3.61	Cr	2.05	1.7	1400	280	Black; adherent
1.08	Cu	0.75	1.1	1400	240	Black; adherent
3.60	Cu	2.53	0.78	1400	240	Black; adherent
1.09	Fe	0.67	3.0	520	250	Gold-gray; adherent
3.95	Fe	2.46	2.4	1400	320	Gray; adherent
1.03	Hf	2.00	1.4	1400	270	Black with raised edges; adherent
4.08	Hf	7.65	1.4	1400	260	Black with raised edges; adherent
1.03	Mo	1.08	2.5	1400	340	Black with raised edges and white spots; adherent
0.91	Ni	0.59	1.5	1400	260	Black; adherent
4.22	Ni	2.75	1.0	1400	240	Gray (gold tinge); adherent
1.08	Pt	2.28	1.5	1400	270	Black; adherent
0.80	Si	0.25	3.4	1400	340	Gray with white specks on faces; adherent
0.89	U	2.30	3.2	1400	240	Black with raised edges; 2 faces gold flaky oxide
0.68	W	1.34	1.9	3000	390	Black; adherent
1.96	W	3.87	3.6	1400	370	Black with yellow adherent oxide at flaws in metal; adherent

num foil (weighing before and after) and placed in a vertical tube furnace at $700^{\circ}\text{C} \pm 4^{\circ}\text{C}$. Oxygen was dried over Molecular Sieve and passed slowly through the chamber after initial flushing. The specimens were weighed periodically until they had oxidized to the point where the platinum wrapping had swollen and burst with the release of some of the oxide. Consequently, the last few points represented a fairly thick oxide layer which diminished the effective specimen area exposed to oxygen. This effect was counterbalanced to an unknown extent by surface roughening which accompanied the appearance of non-adherent oxide.

RESULTS

The plots of weight gain vs. time are given in Figures 1 to 22 inclusive. Log-log paper was used to identify transitions in the rates.

Wherever possible, the curves or portions of the curves were fitted first to slopes of 0.33, 0.50 or 1.0. In the case of the cubic law the slope of 0.33 was a good fit for the initial portion of eight out of twenty-two curves. The remaining curves were fitted best by slight deviations from the cubic law which are indicated on the figures.

In the transition region an attempt was made to fit the data to a parabolic slope in accordance with the theory of Smeltzer. This could be done in some fashion for eleven out of the total of twenty-two curves. Ten curves showed no evidence of a parabolic region and one (4 a/o Cu) showed a slope of 0.44 at the time the experiments were ended.

Following the above approach the curves were grouped into arbitrary classes shown in Table II. The first class showed a cubic to linear transition (4 a/o Fe is included here); the second showed changes from cubic to parabolic to linear and the third showed no definite transition. The data are grouped in terms of increasing times to transition so that the alloys corroding most rapidly appear at the top of the table while those corroding least rapidly appear at the bottom.

The early points for times up to 30 minutes were weighted less heavily in drawing a curve for the volumetric data. The transitions were considered to be the first break in the curve rather than the intersection of the initial and final slopes. As pointed out by Cox¹⁷ the log-log plot can be deceptive because a slope of 1.0 is only observed when the curve on the linear plot intersects the origin. Thus, it is ^{not} possible to decide from the log-log plots whether the oxidation rate has become linear or not.

The curve for 4 a/o Fe showed several breaks indicating multiple transitions. A number of the other curves also indicated changes of this type such as 1 a/o Cu but to a lesser extent. Linear plotting would be expected to show these changes more clearly.

TABLE II

Times to Transition During the Oxidation of Zirconium
and Zirconium Alloys in Oxygen (1 Atm., 700°C)

Alloy (Atom Per Cent)	Initial Slope of Log-Log Plot	Time (Min.)	Comments
0.80 Si	0.37	450	Cubic to Linear Transition
0.65 C	0.36	460	" " " "
1.96 W	0.32	800	" " " "
0.90 Be	0.27	2,000	" " " "
1.08 Pt	0.33	2,500	" " " "
3.61 Cr	0.33	2,600	" " " "
4.23 Be	0.30	3,300	" " " "
1.03 Mo	0.36	4,000	" " " "
3.95 Fe	0.33	3,700	First of Several Transitions
Unalloyed Zr	0.33	2,000	Cubic to Parabolic (Followed by Linear)
4.08 Hf	0.36	2,500	" " " " " "
1.03 Hf	0.35	3,000	" " " " " "
1.09 Fe	0.34	4,000	" " " " " "
0.77 Cr	0.33	5,000	" " " " " "
0.91 Ni	0.35	5,000	" " " " " "
0.86 Co	0.34	5,000	" " " " " "
0.89 U	0.36	5,000	" " " " " "
3.72 Co	0.33	7,000	" " " " " "
0.68 W	0.35	~10,000	" " " " " "
1.08 Cu	0.35	No Def. Trans.	Final Slope (300,000 min.) = 0.65
4.22 Ni	0.33	" " "	" " " " = 0.5
3.60 Cu	0.33	" " "	" " " " = 0.44

FIG. 15-1. Weight Gain of Zirconium-0.25 Wt.% Si Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-2. Weight Gain of Zirconium-0.086 Wt.% C Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-3. Weight Gain of Zirconium-3.87 Wt.% W Alloy
in Oxygen at 1 Atm., 700 C.

FIG. 15-4. Weight Gain of Zirconium-0.09 Wt.% Be Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-5. Weight Gain of Zirconium-2.28 Wt.% Pt Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-6. Weight Gain of Zirconium-2.05 Wt.% Cr Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-7. Weight Gain of Zirconium-0.44 Wt.% Be Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-8. Weight Gain of Zirconium-1.08 Wt.% Mo Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-9. Weight Gain of Zirconium-2.46 Wt.% Fe Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-10. Weight Gain of Unalloyed Zirconium in Oxygen at 1 Atm., 700 C.

FIG. 15-11. Weight Gain of Zirconium-7.65 Wt.% Hf Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-12. Weight Gain of Zirconium-2.00 Wt.% Hf Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-13. Weight Gain of Zirconium-0.67 Wt% Fe Alloy
in Oxygen at 1 Atm., 700 C.

FIG. 15-14. Weight Gain of Zirconium-0.44 Wt% Cr Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-15. Weight Gain of Zirconium-0.59 Wt.% Ni Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-16. Weight Gain of Zirconium-0.55 Wt.% Co Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-17. Weight Gain of Zirconium-2.30 Wt.% U Alloy
in Oxygen at 1 Atm., 700 C.

FIG. 15-18. Weight Gain of Zirconium-2.44 Wt.% Co Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-19. Weight Gain of Zirconium-1.34 Wt.% W Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-20. Weight Gain of Zirconium-0.75 Wt.% Cu Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-21. Weight Gain of Zirconium-2.75 Wt.% Ni Alloy in Oxygen at 1 Atm., 700 C.

FIG. 15-22. Weight Gain of Zirconium-2.53 Wt.% Cu Alloy in Oxygen at 1 Atm., 700 C.

To facilitate comparison with the other alloys studied by Porte a resume of his data is presented in Table III. The alloys are arranged in order of increasing time to transition. It is apparent that transition is not limited to alloys which followed the cubic law. In the case of the 3.54 a/o Ta alloy the pre-transition slope was 0.60.

DISCUSSION

By prolonging exposure to oxygen up to 200 days it was possible to find transitions in all the alloys studied by Porte with the exception of those containing copper and nickel. Therefore, transition appears to be the rule for zirconium base alloys with these alloys as possible exceptions.

Based on the oxidation curves up to 1400 minutes three binary systems had lower cubic oxidation rates than zirconium, viz. the Be, Cu, and Ni alloys. The prolonged exposures showed that the beryllium alloys exhibited shorter transition times than unalloyed zirconium in contrast to the copper and nickel alloys. Therefore, the pre-transition slopes seem to be unrelated to the times for appearance of transition.

Only two alloys appeared to be suitable for a test of Smeltzer's theory. These were 4 a/o Ni and 4 a/o Cu shown in Figures 21 and 22, respectively. In view of the other data there was little to be gained by curve-fitting in only two cases. It is felt, however, that a detailed examination of the oxide on these alloys should be made in comparison with unalloyed zirconium. Metallographic examination of these alloys did not show any particular characteristics distinguishing them from the other alloys.

In comparing the results of this study with the results of other investigators the authors were led to certain conclusions suggesting a new theory of the cubic law of oxidation. The basic postulate of this theory is that the migration processes through the oxide decrease as the compressive stresses in the oxide layer increase.

On the basis of this assumption one may write:

$$\frac{dx}{dt} = \frac{K_1}{x} - \left(\frac{K_2}{S} \right)$$

where x = oxide thickness

t = time

S = the stress within the oxide

K_1 and K_2 are constants.

If S is independent of x then the parabolic law is obeyed. If S is a function of x then the growth law will deviate from the parabolic law. Assuming

TABLE III

Times to Transition During the Oxidation of
Zirconium Alloys in Oxygen (200 mm 700°C).

Data of Porte, et. al.⁽⁹⁾

Alloy (Atom Per Cent)		Slope of Log-Log Plot	Time to Transition (Min.)	Alloy (Atom Per Cent)		Slope of Log-Log Plot	Time to Transition (Min.)
3.60	Si	0.39	6	1.84	V	0.41	120
3.62	Al	0.29	7	0.96	Sn	0.28	235
4.00	Pb	0.28	7	3.54	Ta	0.60	270
3.60	Sn	0.31	20	0.58	Pb	0.28	273
3.72	C	0.46	23	4.16	Ti	0.43	275
2.15	Al	0.33	24	0.60	Nb	0.36	365
1.42	Al	0.36	25	1.08	Ti	0.37	370
1.62	Pb	0.30	34	2.12	Ti	0.39	385
2.34	Mo	0.35	40	1.82	Nb	0.46	500
1.64	C	0.41	48	3.52	U	0.35	530
3.82	Nb	0.35	49	1.01	V	0.35	530
3.65	Mo	0.36	64	2.04	Pt	0.32	630
1.68	Sn	0.32	111	4.22	Pt	0.31	655
1.94	Si	0.43	115				

that

$$S = K_3 x^n \text{ and } n = 1$$

then $\frac{dx}{dt} = \frac{K_1 K_2}{K_3 x^2} = \frac{K_4}{x^2}$

which is the cubic law.

Deviations from the cubic law are readily explained if $n \neq 1$ or if $\frac{dx}{dt}$ is not exactly proportional to $\frac{1}{x^2}$. In the oxidation of zirconium the EMF of the growing scale is approximately one-half the theoretical EMF, indicating that the ionic and electronic resistances are equally important in controlling the rate. An inverse dependence of either resistance upon stress would give rise to a cubic law.

According to the stress theory the oxide on a metal following the cubic law will be in a state of compression. It is assumed that some form of stress relief occurs whenever the oxidation rate changes to a parabolic or linear function of time. As evidence to support this viewpoint a review of experimental data on the oxidation of zirconium is presented in Table IV.

All investigators who used relatively thin specimens and high temperatures found that their data were closer to a parabolic relationship than to a cubic. Both of these conditions will favor stress-relief in the growing oxide layer because of the low mechanical strength of the metal substrate. The existence of high compressive stresses within the oxide is substantiated by the growth phenomena observed by Baldwin⁷ and by Herenguel.¹⁸ As Baldwin pointed out, the interpretation of growth is complicated by a number of incongruous observations but the existence of biaxial compressive stresses in the oxide film is the starting point for any acceptable explanation.

The thinnest foils which were studied were 0.005 in. thick (0.0127 cm). These specimens followed a parabolic law except where the surface was mechanically polished to 4/0 paper in the study of Gulbransen and Andrew⁶ (450 to 550°C) and in the study of Charles, Barnartt, and Gulbransen⁸ (350 and 450°C). Thin foil (0.015-0.022 cm thick) was also studied by Sensell¹¹ for the comparatively short times of 20 to 400 sec. at 400°C and 20 to 7000 secs. at 500°C with the rate law approaching cubic at the end of the 500°C measurements. Thicker foils (0.009 and 0.030 in.) were also observed to follow the parabolic law in the temperature ranges of 600-946 and 700-1100°C, respectively.

The most thorough investigations showing the cubic law were those of Belle and Mallett⁴ and Porte, Schnizlein, Vogel and Fischer.⁹ The former investigators used cylinders and the latter used rectangular blocks. The temperature ranges were 575-950°C and 400-900°C, respectively. The only investigator to use spheres was Sense,¹¹ but his conditions were too restricted to be of much value.

TABLE IV

The Reaction of Zirconium with Oxygen
Results of Various Investigators

Investigators	Temperature Range (°C)	Pressure (torr)	Specimen Shape and Size	Polishing Technique	Rate Law Observed	Activation Energy (kcal/mole)
(1) Gulbransen and Andrew	200-425	76 (small pressure dependence 0.76 to 76)	Foil 0.005 in. thick	Mechanical (4/0 paper wet with kerosene)	Parabolic	18.2
(2) Cubicciotti	600-920	200 (no pressure dependence 1-200)	Foil 0.0054 in. thick	"rubbed shiny"	Parabolic	32
(3) Fassel	600-946	1 atm. (no pressure dependence from 1-35 atm at 700°C)	Foil 0.009 in. thick	Mechanical as-rolled	Parabolic	30.4
(4) Belle and Mallett	575-950	1 atm.	Cylinders 0.7 cm diameter x 4 cm 1.4 cm diameter x 5 cm	Mechanical 600-grit silicon carbide wet with kerosene	Cubic	47.2
(5) Garibotti, Green and Baldwin	700-1100	1 atm.	Sheet 0.030 in. thick	Mechanical (3/0 paper)	Parabolic, slopes of 0.43 to 0.46	—
(6) Gulbransen and Andrew	400-700	76	Foil 0.0127 cm thick	Chemical (HNO ₃ -HF-H ₂ O)	Parabolic (deviation above 600°)	28.6
	450-750 Ignition 800	76	Foil 0.0127 cm thick	Mechanical (4/0 paper)	Cubic (deviation above 550°)	—
(7) Kofstad	650-1100 Linearly Increasing Temperature 2.22°C/min.	Pressure and specimen data not given			Cubic (650-950° C) Parabolic (950-1100° C)	48 60
(8) Charles, Barnartt and Gulbransen	350 and 450°C	1 atm.	0.012 x 2.0 x 3.0 cm	Mechanical 4/0 paper wet with kerosene	Cubic	38
(9) Porte, Schnizlein Vogel and Fischer	400-900°C	50,200,800 (no pressure dependence)	1 x 1.5 x 2 cm (Also cold-rolled foil 0.010 in. thick)	Mechanical 600-grit	Cubic, slopes of 0.29 to 0.39 (av. 0.34) (0.35 for the foil)	42.7
(10) Osthagen and Kofstad	800°C	1 atm.	0.5 x 10 x 20 mm	Not specified	Cubic initially	—
(11) Sense	400 and 500°C	12-83	Spheres 0.51 to 0.52 cm diameter and Foil 0.015-0.022 cm thick	Mechanical, 3/0 paper followed by diamond dust or Chemical (HNO ₃ -HF-H ₂ O)	At 400°C slope changes from 0.76 to 0.51 At 500°C slope changes from 0.7 to 0.51 to 0.36	29.3 42 (Parabolic) (Cubic)

An interesting difference based on surface preparation was found by Gulbransen and Andrew⁶ using 0.0127 cm foil. Etching with HF-HNO₃ yielded a parabolic dependence in the temperature range of 400 to 600°C while polishing to 4/0 paper gave a cubic dependence from 450 to 550°C. It is possible that an oxide stress-relief mechanism operated in the former case and not in the latter. Kendall¹⁹ showed that a thin plate which was polished on one side and rough ground on the other curved during oxidation in air with the smooth surface on the convex side. It is possible that the etching used by Gulbransen approximated a polished surface and led to expansion of the surface.

None of the above investigators noticed growth in their specimens with the exception of Garibotti, Green and Baldwin⁷ who noted increases in oxygen of 2 and 3%. These changes are relatively small and would be expected to escape notice unless attention were given to this point. Consequently, the absence of commentary on "growth" does not mean that it was not a factor in the observed experiments.

Stress as a factor in oxide growth can also explain some other aspects of zirconium oxidation such as the effect of vacuum annealing, the "memory" phenomenon, and the sensitivity to surface preparation. The first two effects have only been studied for oxidation in water or water vapor but the pattern of oxide growth is sufficiently similar to be considered here.

The influence of vacuum annealing was first pointed out by Misch²⁰ who found that heating for 1 min. in vacuum at 600°C was sufficient to cause a temporary increase in corrosion rate in 350°C water. On the other hand a very short heating at 600°C did not produce an effect on the weight gain curve despite a large increase in conductivity of the oxide. It is now believed that readjustment of the vacancy gradient in the oxide occurs rapidly and the necessity for longer vacuum annealing times is related to stress relief in the oxide layer. This same interpretation is suggested for the results of Kass and Scott²¹ who vacuum annealed specimens of Zircaloy-2 at 590°C and 700°C after corroding in 360°C water. The subsequent oxidation curve showed a large increase in rate which persisted for many days.

The "memory" phenomenon as observed by Thomas and Kass²² is associated with transfers of corrosion specimens from one temperature to another with temporary retention of the original corrosion rate. The effects were more noticeable in the pre-transition region, and Thomas suggested that changes in the vacancy gradient were the most likely explanation of these effects. According to the stress-controlled oxidation theory the "memory" effect is a readjustment of the migration processes in the oxide layer as a result of changing stresses in the oxide.

It is possible that the oxide layer on zirconium can develop in a stressed or non-stressed condition dependent on surface work, fluoride contamination and small amounts of critical elements such as titanium. Examination

by electron microscopy is probably the best approach to understanding some of these problems. The effect of tensile stresses on oxidation also may be valuable in studying the pre-transition condition.

Another approach is to determine the EMF of the growing oxide scale on foil and on massive zirconium. If foil permits greater stress relief then a change in ionic or electronic conductivity should be reflected in a change in the EMF.

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SOME EFFECTS OF PRESSURE ON THE OXIDATION
OF ZIRCALOY-2 IN STEAM AND OXYGEN

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SOME EFFECTS OF PRESSURE ON THE OXIDATION
OF ZIRCALOY-2 IN STEAM AND OXYGEN

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Abstract

Experiments under constant pressure conditions show that the oxidation of zircaloy-2 in steam or oxygen is relatively insensitive to pressure. When the pressure is changed during the course of post-transition oxidation, however, the rate of oxidation is observed to change proportionately with the change in pressure. Subsequently the rate of oxidation recovers and eventually attains a rate close to that prior to the changing of the gas pressure.

This behavior is difficult to reconcile with the concept of an oxide diffusion barrier of constant thickness which controls the linear post-transition oxidation rate. Alternative mechanisms are discussed and it is concluded that the post-transition oxidation rate at any temperature may be determined by the rate of oxidation of non-stoichiometric ZrO_2 at that temperature. The possibility of performing experiments to test these suggestions is considered.

Introduction

The dependence on pressure of the oxidation of unalloyed zirconium in steam is well established.^(1,2) The evidence that is available for zircaloy-2, however, shows that pressure apparently has only a slight effect on both the pre-transition⁽³⁾ and post-transition oxidation in steam. No systematic study has been reported previously of these apparently small effects of pressure on the oxidation of zircaloy-2.

In a recent study of the oxidation of niobium,⁽⁶⁾ the pressure dependence of the oxidation rate was measured by a continuous recording of the weight of a sample using Sartorius "electrono" microbalances. The gas pressure was changed suddenly during the course of the oxidation, and the change in the rate of oxidation was measured from the short length of recorder chart on either side of the point at which the pressure change took place. This method had the advantages of rapidity, since a series of pressure changes could be made rapidly during the same experiment, and of selectivity, since the pressure dependence of the oxidation curve could be measured at several points during the same experiment with the oxide film thickness remaining effectively constant during each determination.

Experiments (at constant pressure) with zircaloy-2 showed the anticipated small effect of pressure, but these effects were largely obscured by experimental variations from specimen to specimen. It was decided, therefore, to carry out a study of the pressure dependence of the oxidation of zircaloy-2 using the method developed for niobium oxidation. By this means, variation from specimen to specimen could be eliminated and both pre- and post-transition oxidation could be examined separately.

Experimental Method

Experiments in 'specpure' oxygen at pressures up to about 50 cm Hg, and in water vapour at pressures of 1-2 cm Hg were performed using two Sartorius "electrono" vacuum microbalances.

Experiments in steam at atmospheric pressure were performed in flowing steam apparatus of the type described previously.⁽⁷⁾ Experiments at 500 psi. were performed either in sealed silica ampoules, to which the appropriate quantity of water had been added before sealing under vacuum, or in stainless steel autoclaves of one of the types described previously.⁽⁸⁾

Specimens were cut from an 0.030" sheet of zircaloy-2 (Billet Z8006) and were abraded to 4/0 emery and pickled before oxidation.

Results

The weight gains of specimens in experiments at constant pressures of 15 mm. Hg, 1 atm. and 500 psig. of steam or water vapour are shown in Fig. 1. Any small differences between the results at the two higher pressures are lost in the experimental scatter, however the curve at 15 mm. Hg appears to be definitely below that of the other two.

Experiments in both steam and in oxygen at 500°C showed a small dependence of the pre-transition oxidation on pressure, the magnitude of the effect being about the same as that observed for unalloyed zirconium in oxygen by Gulbransen and Andrew.⁽⁹⁾ Also in agreement with these authors, a larger effect of pressure was observed in the very thin film region, (Fig. 2).

Although little effect of pressure was observed during post-transition oxidation under isobaric conditions, large changes of rate were observed during experiments in oxygen in which the pressure was changed instantaneously. The results of carrying out a series of pressure changes on one specimen at short time intervals (the procedure adopted for niobium) were inconsistent. This was due to the fact that the rate of oxidation after a pressure change was not linear. When the specimen was allowed to reach equilibrium after each change of pressure it was found that the rate of oxidation returned approximately to the original oxidation rate. This behaviour is shown diagrammatically in Figure 3. From the curves obtained in this way, it was possible to plot both the instantaneous (Fig. 4) and the equilibrium (Fig. 5) dependence of the oxidation rate on the pressure. The good agreement between the "equilibrium pressure dependence" (Fig. 5) and the points in the same figure obtained from experiments under isobaric conditions shows the "recovery" of the oxide film, after a pressure change, genuinely represents an attempt to return to the condition in which it would have been had it been oxidised at the new pressure from the start of the experiment. The manner in which the pressure dependence develops during the transition process is shown in Figure 6.

The effect of pressure on the parameters of the zircaloy-2 oxidation

FIG. 16-1. OXIDATION OF ZIRCALOY - 2 IN STEAM AT 500°C. AND CONSTANT PRESSURE.

5-91 FIG. 16-2. EFFECT OF PRESSURE ON THE GROWTH OF THIN OXIDE FILMS ON ZIRCALLOY-2 AT 300°C.

ZIRCALOY - 2

- A TRANSITION POINT
 BCQ POST-TRANSITION RATE
 C PRESSURE RAISED ($P_2 > P_1$)
 E PRESSURE REDUCED ($P_3 < P_2$)
 t_1 TIME TO TRANSITION
 $t_2 - t_1$ TIME FOR TRANSITION TO BE COMPLETED
 $t_4 - t_3$ TIME TO REACH EQUILIBRIUM RATE AFTER A
 $t_6 - t_5$ CHANGE OF PRESSURE
 $R_1(Q)$ POST-TRANSITION OXIDATION RATE AT P_1
 $R_2/R_1, R_3/R_4$ INSTANTANEOUS PRESSURE DEPENDENCE
 R_3 POST-TRANSITION OXIDATION RATE AT P_2
 $R_3/R_1, R_5/R_3$ EQUILIBRIUM PRESSURE DEPENDENCE

WEIGHT GAIN

FIG. 16-3. OXIDATION CURVE OBTAINED BY CHANGING STEAM OR OXYGEN PRESSURE

FIG. 16-4. INSTANTANEOUS PRESSURE DEPENDENCE OF ZIRCALOY-2 OXIDATION.

FIG. 16-5. EQUILIBRIUM PRESSURE DEPENDENCE OF ZIRCALOY-2 OXIDATION.

FIG. 16-6. DEVELOPMENT OF PRESSURE DEPENDENCE DURING ZIRCALOY-2 OXIDATION.

curve in oxygen is shown in Table 1. The negligible effect of pressure on the pre-transition oxidation behavior is shown by the small variation in the time to transition and the weight gain at transition. A tendency towards both increasing time and weight gain at transition with decreasing pressure is not incompatible with this situation.

Both the time to reach equilibrium after transition and the weight change during transition vary very considerably. Any evidence of a tendency for the time to increase with decreasing pressure is apparently lost in the variation from specimen to specimen. This is not surprising since the transition process involves a propagation step which is known to be very dependent on physical effects, such as geometry. In an experiment in steam at 500°C the time to transition and weight gain at transition differed very little for plate and spherical specimens. The time to reach the equilibrium oxidation rate after transition, and the weight gain at this point, changed from 9 days and 240 mgm/dm² to 37 days and 680 mgm/dm² in the same experiment.

Similarly the time to reach equilibrium after a pressure change, and the weight change during this process are very variable. The time shows a tendency to increase with decreasing pressure, and the weight change is (with few exceptions) of about the same size as that prior to the transition point.

Experiments in steam show the same general behaviour, but because weight gains, at pressures other than ~15 mm. Hg could only be measured discontinuously it was impossible to obtain an accurate plot of the instantaneous pressure dependence. The equilibrium pressure dependence in steam follows the shape of the oxygen curve quite closely, although the post-transition oxidation rates in steam and oxygen at 600°C are not identical.

The experiments in oxygen were carried out with relatively small changes in pressure (X4); the results of an experiment in which a large pressure change was employed are shown in Figure 7.

Experiments in which an inert gas (nitrogen or argon) was added to experiments in oxygen, after either a pressure increase or decrease, showed that the transient effects following a pressure change were not due to any

FIG. 16.7. RATE OF OXIDATION AFTER A LARGE PRESSURE CHANGE

TABLE 1. EFFECT OF PRESSURE ON THE PARAMETERS OF THE ZIRCALOY-2 OXIDATION CURVE (see Fig. 3)

Experiment	Initial Oxidation Curve					$P = \frac{1}{4}P_1$			$P = 4P_1$			$P = P_1$		
	P_1	t_1	A	$t_2 - t_1$	B	Δt	step	Δw	Δt	step	Δw	Δt	step	Δw
	mm/hg	hours	mg/dm ²	hours	mg/dm ²	equi- librium hours	height mg/dm ²	equi- librium hours	equi- librium hours	height mg/dm ²	equi- librium hours	equi- librium hours	height mg/dm ²	equi- librium mg/dm ²
159	10	6.0	53.9	21.0	154.1	-	-	-	1.73	5.23	24.1	15.4	21.5	39.3
156	20	5.5	52.4	11.5	129.8	15.7	34.8	51.9	-	-	-	2.2	7.0	32.2
157	20	5.5	55.8	17.0	197.2	-	-	-	2.36	10.3	45.0	14.8	69.8	152
155	40	4.5	46.4	9.0	114.5	11.5	35.8	59.3	-	-	-	2.33	11.6	43.6
163	40	5.75	55.3	11.0	117 +	-	-	-	1.77	6.9	30.5	16.5	61.0	160
158	80	4.5	41.3	15.5	158.8	16.0	41.3	99.0	-	-	-	2.2	13.9	49.4
160	80	3.5	50.4	31.0	432	-	-	-	1.13	16.05	39.3	16.0	90.3	200
162	160	6.0	49.8	12.0	149	10.2	39.5	56.7	-	-	-	1.83	9.36	38.5
152	160	2.55	43.4	2.25	119	-	-	-	-	-	-	-	-	-

Note: All experiments (except 152) follow this pattern:

- 1) Oxidize at 600°C in oxygen until equilibrium is reached after transition.
- 2) Raise or lower pressure by a factor of 4 and continue to equilibrium.
- 3) Return pressure to original value and continue to equilibrium.

mechanical effects in the oxide. No change was observed in the rate resulting from the oxygen partial pressure alone, apart from a very short transient increase in rate. Also, the oxidation rate did not rise immediately following an addition of oxygen to an oxygen/inert gas mixture. These effects are shown in Figure 8 (not to scale).

Discussion

The significance of these results is best discussed in terms of various mechanisms which may be postulated as controlling the post-transition oxidation rate.

(a) The barrier layer hypothesis

Previous investigators have assumed, with few exceptions, that the post-transition oxidation behaviour of zircaloy-2 is controlled by a constant thickness oxide diffusion barrier. The rate of conversion of this oxide to non-protective white oxide is presumed to be balanced by the rate of formation at the metal-oxide interface. A thin layer of black oxide, visible on micrographs, between the outer white oxide film and the metal substrate is generally equated with the supposed barrier layer.

Such a barrier layer would not permit an instantaneous linear increase in oxidation rate following an increase in pressure, however. The characteristics of the pressure dependence of diffusion through such a barrier would probably be similar to those observed for the pre-transition oxidation behaviour. The observed behaviour following a pressure change cannot be explained by adsorption effects in the oxide film, since, even allowing a very large factor of the surface area of the porous outer oxide, the step-heights which are observed are very much larger than the weight gains which would be associated with the adsorption of a monolayer of oxygen on the oxide.

The linearity of the pressure dependence of the oxidation rate following an instantaneous change in pressure is reminiscent of the behaviour of niobium; in the latter case this was shown to be associated with flow of the reactant through the "porous plug" formed by the outer oxide.⁽⁶⁾ It is suggested that the same explanation applies to zircaloy-2. Some sort of equilibrium must exist between the rate of oxidation and the rate of transport through the porous oxide to account for the progressive return of the oxidation rate

FIG. 16.8. EFFECT OF INERT GAS ADDITIONS ON TRANSIENT EFFECTS FOLLOWING A PRESSURE CHANGE.

(after a pressure change) to its original value. This recovery mechanism is probably associated with the growth of fresh oxide since a weight gain of approximately 70 mgm/dm^2 takes place during the attainment of equilibrium after a pressure change, compared with an average weight gain of 50 mgm/dm^2 up to the transition point. This fresh oxide has porosity which differs from that of the oxide formed previously in such a direction as to change the flow rate of the reactant in the desired direction. Thus it would be expected that the oxide formed in oxygen or steam at high pressure would be less porous than that formed at low pressure, in order to produce films giving approximately the same gas flow through them. The occurrence of such variations in porosity have been confirmed by capacity measurements. (10)

The effects observed in oxygen/inert gas mixtures may be explained by accumulation of inert gas or oxygen in the pores adjacent to the metal-oxide interface depending upon the cycle of events taking place. However, calculations of the pore volume from figures for the size of the small transients give values larger than that of the oxide as a whole. Nevertheless, following a drop in oxygen pressure, greater increases in porosity should be required in a gas mixture than in pure oxygen to enable adequate mixing of the gas in the pores. The porosity of the oxide formed in an oxygen/inert gas mixture should therefore be greater than in the presence of oxygen alone (at the same partial pressure). Conversely, on adding further oxygen to an oxygen/inert gas mixture time is required for this to diffuse up to the metal/oxide interface, and hence a short incubation period is observed.

(b) Control by porosity in the oxide film

Having dispensed with an oxide diffusion barrier as the rate controlling factor during post-transition oxidation, an alternative must be provided. It is possible that the flow of reactant through the pores in the oxide represents the rate controlling step; however, there are several reasons which suggest that the porosity of the outer oxide is not rate controlling during constant pressure oxidation, but merely exerts its influence during the transient period following a change in pressure.

The first of these reasons is the very fact that the porosity following a pressure change alters in such a direction as to minimise that pressure change. This behaviour suggests that the porosity of the oxide is merely

in equilibrium with some other factor which is controlling the oxidation and changes in concert with this.

Secondly, during the post-transition oxidation of niobium, which is believed to be controlled by the porosity of the outer oxide, the development of the pressure dependence can be followed from the onset of transition. It is found that during the growth of the porous outer oxide the oxidation rate passes through a maximum then decreases as the porous film thickens, and finally becomes linear when the porosity of the outer oxide has reached its equilibrium value. This type of behaviour is not observed with zircaloy-2; no noticeable maximum occurs in the post-transition oxidation curve at high temperatures. The instantaneous pressure dependence appears early in the transition process and has reached its limit before transition is complete. During the development of the pressure dependence in zircaloy-2, therefore, the oxidation is accelerating not decelerating. It is most likely therefore that the instantaneous pressure dependence arises from some aspect of transition process, and does not play any part in determining the oxidation rate unless the conditions are suddenly changed.

(c) Control by other processes

Two processes which occur during the oxidation of zircaloy-2, and which might be rate controlling, are the oxidation of oxygen-saturated metal to non-stoichiometric oxide, and the oxidation of non-stoichiometric to stoichiometric oxide. The rate of the first of these processes is probably closely represented by the oxidation rate at zero film thickness. A study of the initial oxidation rates in our experiments shows that these are very much greater than the post-transition rate; but this process may represent the limiting rate following a very large pressure change (Fig. 7).

Two studies of the rate of oxidation of non-stoichiometric to stoichiometric oxide have been reported.^(11,12) The latter has become available only recently, and it is the former which has been used here for a comparison with the post-transition oxidation rates of zircaloy-2. Aronsen⁽¹¹⁾ measured the rate of oxidation of non-stoichiometric ZrO_2 gravimetrically, and considered that his results indicated this process to be diffusion controlled. The diffusion coefficients calculated from these results were too low, by several orders of magnitude, to account for the observed oxidation rates of metallic

zirconium. His experiments were performed on "unsized" samples of powder containing a wide range of particle sizes, however, and the surface areas quoted apply only to the initial oxidation rate. It is probable that, at least in part, the shape of Aronsen's curve was due to the decreasing surface area for the reaction. If we use Aronsen's data at the origin to estimate the rate of oxidation and plot these results against the post-transition rates of zircaloy-2, the curves shown in Figure 9 are obtained. These show that Aronsen's results still give rates less than the post-transition rate of zircaloy-2, although the two curves converge at temperatures above 600°C.

However, the post-transition oxidation rates for zircaloy-2 were calculated using the geometrical surface area of the specimen. In fact, the oxide film is porous under these conditions, and the interface at which conversion of non-stoichiometric to stoichiometric oxide is taking place will be considerably larger than the geometrical area of the specimen. Thus, the factorial difference between the curves in Figure 9 may represent the ratio of the reacting interface to the geometrical area of the specimen. That this ratio should decrease with increasing temperature is in accord with the observation that the density of cracks in the post-transition oxide (visible by electron-microscopy) decreases with increasing temperature. (13)

(d) A mechanism for the oxidation transition

During the pre-transition oxidation period conversion of non-stoichiometric to stoichiometric composition proceeds at the outer interface of the oxide, and since oxidation is here controlled by diffusion through a non-porous oxide, it is based on the geometrical area of the specimen and occurs to only a very limited extent. When cracking of the oxide (or some other process which increases its porosity) occurs at the transition point, oxidation of the non-stoichiometric oxide can take place over a much larger surface area. Since access of reactants down the pores, or cracks, can now take place easily the rate of oxidation increases.

During the growth of the porous oxide the compressive stresses under which the film grows will tend to increase the diameter of the pores (or cracks) in the outer part of the oxide. Eventually an equilibrium will be set up whereby the rate of flow of reactant through the porous film, and hence the rate of formation of non-stoichiometric oxide, will be balanced

FIG. 16.9. THE POST TRANSITION OXIDATION RATE OF ZIRCALOY-2 & ZIRCONIUM
 COMPARED WITH THE OXIDATION RATE OF NON-STOICH. ZrO_2

by the rate of oxidation of this non-stoichiometric oxide. The equilibrium condition of the oxide will vary with pressure, in the direction of decreasing porosity with increasing temperature, since, of the processes in equilibrium, only the flow through the porous oxide will be pressure dependent.

When this equilibrium is disturbed (e.g., by increasing the pressure) the flow of reactant up to the metal-oxide interface is increased, and the rate of production of non-stoichiometric oxide (and hence the oxidation rate) increases up to the limit set by the maximum rate of this reaction (see Fig. 7). The increasing thickness of non-stoichiometric oxide will tend to restrict the access of further reactant until the equilibrium between production and oxidation of non-stoichiometric oxide is set up again. Since the rate of this latter process is probably independent of pressure, the equilibrium oxidation rate should also show little or no dependence on pressure.

Confirmatory evidence for the above hypothesis may be obtained by examining the thickness of the residual black non-stoichiometric oxide layer metallographically before and after a change of pressure. It would be predicted that the thickness should increase following an increase in gas pressure, and decrease after a reduction in pressure. This is the reverse of the effect which would be predicted on a diffusion barrier hypothesis. Further evidence could be supplied by measurements of the porosity of separated post-transition oxide films (as was done for niobium⁽⁶⁾). The presence of pores passing right through the oxide would lend support to the suggestion that the black layer of oxide seen at the metal-oxide interface does not represent a diffusion barrier.

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THE CORROSION OF ZIRCALOY-2 FUEL ELEMENT CLADDING
IN A BOILING WATER REACTOR ENVIRONMENT

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INTRODUCTION

The corrosion properties of Zircaloy-2 has been studied extensively in pressurized water systems by numerous investigators,^(1,2) and the corrosion rate has been established, by autoclave studies, for reactor grade Zircaloy-2 up to water temperatures of 680 F and in steam at 750 F. In the past, reactor fuel element designers have had to use this data without knowing the effect, if any, of boiling water reactor environments on the corrosion rate of Zircaloy-2.

Now through the development of a refined mounting technique for metallography specimens, corrosion studies can be extended to irradiated fuel elements and this extrapolation may no longer be required. The corrosion of Zircaloy-2 cladding on intact and defected fuel elements irradiated in the core of the Vallecitos Boiling Water Reactor was investigated in this manner.

A description of this metallographic technique and some of the corrosion characteristics of Zircaloy-2 cladding in a boiling water reactor are presented in this report.

Fuel Element Fabrication⁽³⁾

The Zircaloy-2 fuel element cladding was produced from magnesium-reduced sponge zirconium, and was alloyed and melted by multiple arc fusion. Chemical analyses of "typical" tubing, as supplied by the vendor, are summarized in Table I. The General Electric specification for nuclear grade Zircaloy-2 is also included for comparison.

The tubing fabrication started with Zircaloy-2 ingots which were forged and cut to form extrusion billets weighing about 150 pounds. After hot extrusion, the resulting tubing was reduced in size by three cold-working operations which were followed by a vacuum anneal. The tubing was finished to a final size of 0.572 inch O.D. with a 0.033 inch wall by cold drawing which provided 15 to 25 percent residual cold work.

Fuel element fabrication proceeded by first welding an end plug, then loading the tube with UO_2 pellets and finally welding the second end plug. The end closure welds were made with an inert-gas tungsten-electrode using helium gas. In addition to a helium-mass spectrometer leak check and x-ray radiography to determine weld integrity, all fuel elements were autoclave corrosion tested at 750 F and 1500 psi for 72 hours. Satisfactory elements were covered with a uniform deep metallic grey zirconium oxide film which was about 1 μ thick. During this autoclave test the cladding also picked up about 20 ppm hydrogen.

Irradiation History

All of these fuel elements were irradiated in the core of the Vallecitos Boiling Water Reactor. During these tests, the reactor was operating with a combination plate fuel and rod fuel core with light water coolant at 1050 psig, 545 F and flowing under natural circulation. The temperature rise through the core was small, since the increased heat content of the coolant was converted into steam as it flowed up through the core at about 3 feet/second. At the maximum reactor power level of 30 mw the coolant conditions were limited to a maximum 1075 psig pressure and 556 F temperature. The coolant sub-cooling was 10 BTU/pound and the steam generation rate was 90,000 pounds/hr.

Water chemistry on the total coolant volume of 5600 gallons was main-

TABLE I
CHEMICAL COMPOSITION OF ZIRCALOY-2 TUBING

Chemical Element	Typical Analysis		G.E. Nuclear Grade Zircaloy-2 Specifications	
	Lot I	Lot II	Minimum	Maximum
Sn	1.50 wt.pct	1.49 wt.pct.	*1.3 wt.pct.	1.7 wt.pct.
Fe	0.13	1.0134	0.07	0.20
Cr	0.10	0.066	0.05	0.15
Ni	0.06	0.053	0.03	0.08
Al	43 ppm	76 ppm		75 ppm
B	--	< 0.5		0.5
C	--	264		500
Ca	--	< 15		30
Cd	--	< 0.5		0.5
Cl	--	< 50		50
Co	--	5		20
Cu	35	26		50
Hf	--	90		200
Mg	10	< 15		20
Mn	49	< 25		50
Na	--	< 10		100
Pb	--	< 10		130
Si	74	< 50		100
Ti	--	< 25		50
V	--	< 5		50
W	--	25		100
H	--	10		80
N	50	36		100
O	--	1160		1500
Zr	Balance	Balance		Balance

* 0.18 to 0.38 wt.pct. total Fe, Cr, and Ni

tained by mixed bed ion exchange systems having the capacity to process all of the condensate at 200 GPM and by-pass coolant at 7 GPM. Normal reactor vessel water conditions were as follows: ph 5.5 to 7.0, oxygen content (feed water) 0.01 ppm (vessel water) 0.25 ppm, resistivity 1×10^6 ohms/cm, solids content 1-12 ppm, chloride content 0.02 ppm and oxygen in the steam 12 ppm.

The fuel element sections examined in this investigation operated at maximum heat fluxes ranging from 95,000 to 296,000 BTU/hr ft²°F. This corresponds to exit steam quality of 1% and 5% respectively. A summary of the irradiation conditions is presented in Table II.

Experimental

The corrosion of Zircaloy-2 cladding on fuel elements irradiated in the core of the Vallecitos Boiling Water Reactor was investigated using a refined metallographic technique to preserve the thin surface films. A mounting method involving vacuum impregnation of the specimen with epoxy resin containing 0.1 micron alumina powder was developed to preserve its edges during the grinding and polishing operation in preparation for subsequent metallographic examination.

Epoxy resin was selected for its excellent adhesive properties and low shrinkage. It was applied to the specimen using vacuum impregnation to allow the resin to gently displace the air and penetrate all the interstices to bond the specimen together. The alumina powder was mixed with the resin to increase its hardness and improve its abrasion resistance so that the mounting material would wear less rapidly and protect the specimen edges during the grinding and polishing operations. The alumina also acted as a filler in the resin, which further decreased the shrinkage in the system. The small particle size, 0.1 microns, was used to eliminate a possible source of scratches during the final polishing operations. The resin was formulated to polymerize at room temperature in about 24 hours. Because the polymerization is an exothermic reaction a relatively long curing time is used to keep the temperature down and minimize the shrinkage from thermal contraction.

By following the above procedure and taking all the precautions to reduce

TABLE II
SUMMARY OF IRRADIATION CONDITIONS AND CLADDING CORROSION

Specimen Designation	Fuel Element Cladding Condition	(1) Days at Elevated Temp. (2)	Max. Heat Flux BTU/hr ft ² °F	Cladding O.D. Temp. °F	Weight Gain mg/dm ²	Total H ₂ PPM	Corrosion Hydrogen (3) % Pick-up	Burn-up MWD/T	nvt x 10 ⁻²⁰ 0.18 mev to 10 mev
DP1-249	I	179	243,000	570	164	74	13	4350	13.2
-250	I	179	296,000	576	166	71	12	5300	16.0
-251	I	179	166,000	563	108	67	18	2980	8.9
DP29-21	I	103	95,000	556	34	26	7	940	3.1
-20	I	103	202,000	566	53	--		2000	6.5
-16	I	103	231,000	569	64	--		2200	7.5
-18	I	103	195,000	566	34	66	56	1925	6.3
-205	D	103	290,000	575	42	--		2860	10.0
DP48-179	D	35	242,000	570	51	253		726	1.5
-284	I	35	166,000	563	34	35	8	489	1.0
-283	I	35	236,000	570	22	39	12	710	1.5
-282	I	35	288,000	575	28	43	12	866	1.8
DP42-252	D	9	115,000	558	14	221		39	0.12
-253	D	9	140,000	560	16	644		46	0.15
-246	D	9	115,000	558	16	71		39	0.12
-247	D	9	140,000	560	12	253		46	0.15
-248	D	9	175,000	564	19	230		58	0.18

(1) I - Intact fuel element cladding where integrity of fuel element is maintained.

D - Defected fuel element cladding where moisture has access to fuel element interior.

(2) Includes 3 days at 750 F steam in autoclave.

(3) Basis: total H₂ ppm - 20 ppm H₂ as fabricated = ppm corrosion H₂ pick-up.

shrinkage of the mounting material, corrosion films less than one micron in thickness were preserved for examination and measurement. On these irradiated fuel cladding specimens all of the preparation from mounting in epoxy resin through grinding and the final polishing stage with 1 μ Linde A was performed in the metallography "hot cell". The details of specimen mounting and preparation are presented in Appendix A.

Visual examination of the specimens in both the as polished and etched conditions at magnifications up to 750X was performed with a metallograph having a shielded stage. The details of corrosion film structure were most apparent after lightly etching the Zircaloy-2 to remove traces of smeared metal at the oxide-metal interface. Bright field and polarized light illumination were both useful in the examination.

Bright field illumination was most useful for film thickness measurements and zirconium hydride distribution. Examination under polarized light revealed the presence of red crud films and microcracks in the zirconium oxide film.

Results

All of the following visual examination results were obtained from transverse sections of irradiated fuel element cladding. The irradiation conditions experienced by each specimen identified in the following photomicrographs is presented in Table II.

Visual examination of pre-transition oxide films revealed them to be thin, continuous films of extremely uniform thickness. Such an oxide film was observed on specimen DP42-246 and is shown in Figure 1. This film is 1 micron thick with a ± 0.1 micron variation and is the result of 9 days at elevated temperature. This fuel element was purposely defected and the corrosion resulting on the interior surface of the cladding was the primary hydrogen contributor to the extensive hydride formation observed. The presence of this hydride at the metal-oxide interface did not appear to effect the continuity of this thin oxide film.

A pre-transition oxide film in a more advanced stage of growth, after 35 days at elevated temperature, is shown in photomicrograph DP48-283 of Figure 1. Although the film remains continuous it is not as uniform as that observed after 9 days at elevated temperature. The average "uniform" film

The Zirconium oxide film with an average thickness of 1μ resulted from 9 days at elevated temperature.

This Zirconium oxide film formed during 35 days exposure at elevated temperature had an average thickness of 1.3μ . Zircaloy cladding section contained 39 ppm hydrogen.

Figure 17-1. PRE-TRANSITION CORROSION FILMS ON ZIRCALOY-2 CLADDING

thickness is 1.3 microns. Local areas of accelerated film growth or more properly oxide penetration measured up to 5.3 microns thick. One such area is shown in Figure 2 as a crescent shaped section in the oxide film. The same area is shown as viewed under bright field illumination and under polarized light to demonstrate that microcracking or cleavage in the film is readily detected under polarized light. Notice that the uniform oxide film is a continuous grey band compared with the crystalline appearance of the thicker oxide film section.

Visual examination of the post-transition oxide films revealed them to be continuous films on the surface of the Zircaloy-2 which were highly irregular in thickness and in shape. The microstructure of these films is shown in Figure 3 and is representative of "fuel element cladding" corrosion films after 179 days at elevated temperature. Photomicrograph DP1-249, a section of the cladding wall at 100X, shows the over-all structure of these oxide films and their size relative to the cladding section.

The structural details of post-transition corrosion films are shown in DP1-249 at 500X magnification. The continuity of the oxide film is readily apparent as is the preferential oxidation of certain surface grains of Zircaloy-2. These grains may be preferentially oriented for accelerated oxidation as was observed by Bibb⁽⁷⁾ (KAPL). They also appear to act as sites to initiate break-away corrosion. The mechanism appears to consist of delamination of the thicker sections of oxide film followed by fracture and spalling of the outside layers. DP1-250, photographed under polarized light, reveals the cleavages in the oxidized grains and the delamination of the oxide corrosion film. At this stage of post-transition corrosion some sections of the original "uniform" oxide film are still intact. These films are generally situated between areas of preferential oxidation and showed little or no evidence of delamination when examined under polarized light. Thickness measurements of these films were used to determine the post-transition corrosion rate.

All corrosion film thickness measurements made during this investigation were performed under the following conditions. The specimen was in the lightly etched condition to delineate the metal-oxide interface. Oxide film thickness

measurements were made using a Filar micrometer eyepiece and the film was observed at 750X under bright field illumination. Under these conditions there was no problem distinguishing between the oxide film and any crud deposit present.

In general, ten thickness measurements were made on the "uniform" oxide film at various points along the circumference of the Zircaloy-2 cladding. These film thickness measurements were reproducible to 0.1 microns. For specimens with corrosion films containing local oxide penetrations, ten areas were also measured to obtain an average depth of penetration.

The uniform oxide film thicknesses were converted to weight gain by using the experimentally determined value of $1 \mu \text{ film} = 15.6 \text{ mg/dm}^2$ which was obtained on autoclave tests with Zircaloy-2 at Bettis.⁽⁴⁾ The autoclave corrosion results on Zircaloy-2 and the corrosion of Zircaloy-2 in a boiling water reactor are shown in Figure 4. Note that the boiling water reactor fuel cladding was autoclave corrosion tested at 750 F and 1500 psi for 72 hours prior to its operation in the reactor at 575 F. Therefore, it is not directly comparable with the Bettis autoclave corrosion data which did not include this treatment.

Discussion

In the Vallecitos Boiling Water Reactor, the power generation varies along the vertical axis of the core as the result of the approximately cosine distribution of the neutron flux. The temperature size through the core is small, about 10°F maximum, since the increased heat content of the coolant is converted into steam as it flows up through the core. Hence, the exterior surface of the fuel element cladding is also essentially operating at constant temperature, within 25°F , which temperature difference is primarily the result of the film coefficient and the heat flux. As a consequence of this environment, each fuel element represents a corrosion test covering a range of neutron fluxes and their corresponding heat fluxes all for the same time at similar elevated temperatures.

Thus, this reactor environment presents an opportunity to investigate the combined effect, if any, of neutron flux and heat flux on corrosion as well as the measurement of the corrosion rate of Zircaloy-2 cladding in a

DP48-283

Zirconium oxide film with a crescent shaped zone of accelerated film growth. The oxide film appears as a continuous system when viewed under bright field illumination.

DP48-283

The same field as above when viewed under polarized light discloses the discontinuities in the film. Notice the crystalline appearance resulting from the microcracks present in the accelerated growth region of the film.

Figure 17-2. LOCAL REGION OF ACCELERATED OXIDATION ON ZIRCALOY-2 CLADDING

DPI-249

Transverse section through Zircaloy-2 cladding wall showing the typical microstructure after 179 days at elevated temperature.

V 11459 Bright Field Etched 100X

DPI-249

Zirconium oxide film microstructure showing preferential oxidation of individual Zircaloy grains

V 11458 Bright Field Etched 500X

DPI-250

Microcracking and delamination of oxide film on Zircaloy-2 cladding

V 11369 Polarized Light Etched 500X

Figure 17-3. POST-TRANSITION CORROSION FILMS ON ZIRCALOY-2 CLADDING AFTER 179 DAYS @ ELEVATED TEMPERATURE

VAL 4077

17-13/17-14

Figure 17-4. CORROSION OF REACTOR GRADE ZIRCALOY-2

boiling water reactor core. With this in mind, each rod was examined at three locations by cutting transverse sections near the bottom, center, and top with eight inch intervals between sections. The irradiation conditions experienced by these three sections was obtained from a gamma activity profile of the fuel element which is a measure of the relative fission product concentration along its length. The gamma activity curve was "calibrated" by uranium burn-up determinations of the fuel at specific locations. In this manner, the axial burn-up distribution along the fuel element and its corresponding integrated thermal neutron flux was obtained for each fuel element examined. The maximum heat fluxes for each fuel rod were obtained from reactor core calculations and were furnished by J. O. Arterburn of Operations Physics.⁽⁵⁾ The heat flux of each section of the fuel element was obtained from the ratio of its gamma activity to the maximum gamma activity of the fuel element. All of the in-pile data presented in Table II was obtained by the above procedures.

The corrosion of reactor grade Zircaloy-2 fuel element cladding in a boiling water reactor is plotted in Figure 4. This data was obtained from seventeen specimens taken from seven fuel elements. Ten of the specimens examined were from intact elements and seven specimens were obtained from defected fuel elements. Excluding the initial three days at 750 F steam in an autoclave, the test durations at elevated temperatures in the reactor were 6, 32, 100 and 176 days. The specimens operated at surface heat fluxes ranging from 95,000 to 296,000 BTU/hr ft² F and at corresponding cladding surface temperatures from 556 to 576 F.

These variations in test conditions probably account for some of the spread in the data obtained at each test time. This is indicated in Figure 4 by plotting the range of weight gain obtained for each test time. As a consequence, any corrosion rates predicted on the basis of this data shall be considered preliminary. However, the data at each test time does lie above the Zircaloy-2 autoclave corrosion data having similar time-temperature history indicating that fuel element cladding corrosion is accelerated in the reactor environment. The conversion of the Zircaloy-2 autoclave corrosion data to obtain a corrosion rate with comparable time-temperature history was performed

by the method presented by Thomas and Kass.⁽⁶⁾

The preliminary corrosion curve for Zircaloy-2 fuel element cladding operating in a boiling water reactor at a surface temperature of approximately 575 F is presented in Figure 4. It is based on microstructural evidence that the initial parabolic corrosion rate was in effect at 35 days and micro-cracking and delamination of the oxide was apparent after 103 days at elevated temperature indicating that transition occurred during this period. The time to transition was arrived at by extrapolating the initial parabolic rate curve and the linear corrosion rate curve to the point of intersection. On this basis, including the pre-irradiation autoclave testing 750 F steam for 3 days, the transition from the parabolic corrosion rate to the linear corrosion rate occurs at approximately 65 days at elevated temperature. This preliminary corrosion curve based on the above interpretation of the existing data will be subjected to review and possible refinement as additional in-pile corrosion data is obtained.

The data were examined for evidence of correlation between the accelerated corrosion rate and the heat flux, with its associated neutron flux, which were not separable under these fuel element cladding corrosion conditions. No correlation between the heat flux-neutron flux combination and weight gain was observed in the data up through 103 days at elevated temperature. After 179 days at elevated temperature a correlation was observed; the higher the heat flux-neutron flux, the greater the weight gain. However, these increases were not proportional and considering all the data this apparent agreement at 179 days is interpreted as being fortuitous. The possibility still exists that the heat flux and/or neutron flux contribution to the corrosion rate is an accumulative one. This contribution may be of secondary importance initially, when the corrosion films are thin, and may become primary contributors for the thicker films resulting from longer times at temperature in a boiling water reactor. Additional corrosion data obtained at greater reactor exposures from cladding such as the Dresden Boiling Water Reactor fuel will be examined and may clarify this point.

Zircaloy-2 cladding sections from both intact and defected fuel elements, which experienced comparable in-pile conditions, were examined

and their microstructures compared. A difference in microstructure was observed as greater concentrations of zirconium hydride were present at the metal-oxide interface on the exterior cladding surface of the defected fuel elements. This did not appear to effect the exterior corrosion films, however, and no difference in microstructure was apparent between films on intact and defected fuel element cladding. From the limited data available, no correlation was observed between a defected fuel element and increased corrosion rate.

The hydrogen content reported in Table II on each specimen was obtained from cladding sections taken immediately adjacent to the surface examined. The total hydrogen content was determined on an NRC Vacuum Fusion Gas Analyzer by using the vacuum hot extraction technique to remove the hydrogen from the cladding specimens following the procedure designated in ASTM (E146-597).

Based on the total hydrogen content, which includes the hydrogen content in the as-fabricated condition prior to autoclaving, the % pick-up of the total hydrogen in general ranged from 17.5 to 26% on the intact fuel elements. Assuming a nominal 20 ppm hydrogen content in the as-fabricated condition the corrected hydrogen content, presumably corrosion hydrogen pick-up, results in pick-up fractions ranging from 12% to 18% on the intact elements. Intact element DP-29 is the exception with hydrogen pick-up fractions of 7% and 56%. There was no evidence in the cladding microstructure to explain this apparent anomaly.

Corrosion films on the interior cladding surfaces of the defect elements were not intact and the total corrosion could not be determined by film thickness measurements. For this reason, the total corrosion hydrogen generation and hydrogen pick-up fractions were not determined for the defect elements.

Conclusions

Zircaloy-2 fuel element cladding corrosion is accelerated in a boiling water reactor environment compared with Zircaloy-2 corrosion having similar time-temperature history in autoclave tests. These preliminary results indicate that the slope of the post-transition corrosion curve for Zircaloy-2

cladding operating in a boiling water reactor at 575 F surface temperature lies between that of 680 F water and 750 F steam for Zircaloy-2 corrosion in an autoclave.

No correlation between the heat flux-neutron flux combination and weight gain was observed in the corrosion of Zircaloy-2 cladding in a boiling water reactor up through 103 days at elevated temperatures. After 179 days at elevated temperature increases in the heat flux-neutron flux resulted in greater weight gains. These increases were not proportional and considering the preliminary nature of the data the apparent correlation at 179 days is interpreted as being fortuitous. These observations are limited to heat fluxes less than 300,000 BTU/hr ft² F and may not be valid for greater heat fluxes and longer times at temperature in boiling water reactor environments.

Based on a nominal 20 ppm hydrogen content in the cladding in the as-fabricated condition the corrosion hydrogen pick-up fractions ranged from 12% to 18% for the intact fuel elements in the boiling water reactor.

ACKNOWLEDGEMENTS

The author would like to acknowledge the contribution of Dr. C. N. Spalaris to the fuel element fabrication data and irradiation history and the efforts of R. E. Smith and W. V. Ketron for the careful metallographic work. Helpful discussion were held with Dr. H. H. Klepfer and R. F. Boyle on the experimental techniques and on the contents of the manuscript and are also gratefully acknowledged.

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APPENDIX A

PREPARATION OF METALLOGRAPHY SPECIMENS FOR OPTICAL MEASUREMENTS OF THIN SURFACE FILMS

The following technique was developed to preserve specimen edges during metallographic preparation to determine the adherent corrosion film thickness on Zircaloy clad reactor fuel elements. This method, which involves vacuum impregnation of the specimen with epoxy resin containing 0.1 micron alumina powder, was readily adopted to the remote handling techniques required for these radioactive specimens. The only special equipment required is a simple vacuum system consisting of a mechanical vacuum pump and a glass bell jar.

The specimen mounting method proceeded as follows:

- A. Add one part of Hysol type 3410 hardener⁽¹⁾ to ten parts by weight of Hysol 2038 epoxy resin. This composition gives a one hour pot life at room temperature and cures over night.
- B. Add an equal volume of gamma alumina abrasive⁽²⁾ to the epoxy resin and mix to a uniform consistency. The amount of the alumina filler may be varied. In general, one must balance the beneficial decrease in shrinkage obtained by the addition of more alumina filler with the corresponding increase in viscosity which results in poorer penetration of mounting resin into the specimen.

The resin-alumina mixture was then transferred into the hot cell and vacuum impregnated into the specimen using the following procedure:

- C. The resin mixture was placed in the bell jar which was then evacuated to degas the resin and remove any air entrapped during mixing.
- D. A standard 1½ inch diameter bakelite metallography mount, which had been bored to form a cup to contain the specimen, was placed in the bell jar. Then enough resin was poured into the cup to cover the bottom. The specimen was positioned in the cup and the system was evacuated for 10 minutes.
- E. The system was brought to atmospheric pressure, more resin, approximately 1/8 inch in depth, was added to the cup and it was

evacuated for another 10 minutes.

F. The bell jar was again brought to atmospheric pressure and the cup filled with resin. The system was evacuated for approximately one half hour or until the bubbling of air from the resin ceases.

G. The bell jar was now brought to atmospheric pressure and the mounted specimens were removed.

The epoxy resin hardened overnight and the specimen was then processed for metallographic examination by abrading through 600 grit silicon carbide papers with water lubrication on a "Buehler Automet". The specimens were then polished with 1 μ diamond paste on a nylon cloth covered "Buehler Automet Polisher." Final polishing was done with an aqueous suspension of alpha alumina on Buehler microcloth using a "Syntron" vibratory polisher.

Surface and edge preservation on specimens prepared in this manner were satisfactory for thickness measurements on films down to the resolution limits of the optical microscope.

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ELECTRICAL PROPERTIES OF ZrO_2 CORROSION FILMS

Interim Report No. 1

ELECTRICAL RESISTANCE MEASUREMENTS

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Chemical Metallurgy Operation
Hanford Laboratories
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Richland, Washington

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Work Performed Under
AEC Contract AT(45-1)-1350

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ELECTRICAL PROPERTIES OF ZrO_2 CORROSION FILMS

Interim Report No. 1

ELECTRICAL RESISTANCE MEASUREMENTS

INTRODUCTION

Zirconium dioxide (ZrO_2) is normally considered to be a very good electrical insulator. However, some of the oxygen atoms in the ZrO_2 lattice can be removed converting the ZrO_2 to formulae such as $ZrO_{1.95}$.⁽¹⁾ The presence of oxygen anion vacancies in the lattice converts the insulating ZrO_2 into an n-type semi-conductor. The corrosion films on zirconium alloys are oxygen deficient structures and would be expected to have semi-conducting properties. Since zirconium corrosion is thought to proceed by oxygen diffusion via these oxygen vacancies, electrical resistance measurements also provide a technique for determining the effect of such variables as alloy content, heat treatment, and radiation effects. It has been determined that gaseous hydriding by H_2 occurs under conditions⁽²⁾ which also produce a highly oxygen deficient corrosion film, so electrical measurements potentially offer a means of detecting a hydrogen permeable corrosion film.

The electrical resistance of ZrO_2 corrosion films are being studied as a function of oxide thickness, alloy content, heat treatment, radiation effects, and hydrogen absorption. As data become available the observed electrical behavior of Zr oxide films will be compared with current theories of zirconium corrosion and hydriding. It is obvious that resistance

measurements would be equally interesting for corrosion films on other materials which form semi-conductive oxides such as p-type oxides where the corrosion process takes place by cation migration.

SUMMARY AND CONCLUSIONS

Measurements have been made of the electrical resistance of ZrO_2 corrosion films on Zircaloy-2 and crystal bar zirconium as a function of variables such as gas atmosphere, radiation, heat treatment and temperature.

It has been found that the electrical resistance of the corrosion film decreases from the meg-ohm region to as low as 10 ohms when the gas atmosphere is made non-oxidizing. This resistance drop has been observed in vacuum, pure helium, and hydrogen. It was noted in the hydrogen experiment that the resistance drop occurred before hydriding began. The decreased film resistance is attributed to an increased concentration of oxygen anion vacancies in the film which also may contribute to hydrogen absorption.

It was found that a log resistance versus $1/\text{temperature}$ plot yields a fairly straight line allowing an "activation energy" to be calculated.

A theory is presented which suggests a lower electrical resistance for the corrosion film may be used to lower corrosion hydrogen absorption. The electrical resistance of the oxide on beta quenched Zircaloy-2 was found to be lower than that of alpha annealed material, correlating with the observation that beta quenched Zircaloy-2 has a lower corrosion hydrogen pickup.

The effect of in-reactor radiation was to lower the ZrO_2 film resistance by a factor of 600. This is indicative of a higher concentration of

vacancies and interstitials in the ZrO_2 film. A higher concentration of vacancies would produce a higher in-reactor corrosion rate, which has been previously observed.

DISCUSSION

Application of Semi-Conductor Theory

Electrical current can be carried through a solid by either mobile electrons or electron "holes." An electron hole is defined as the absence of an electron. Current flow by electron holes occurs as an electron fills an adjacent hole destroying the hole, but creating a new hole where the electron was originally located.* In this manner the hole migrates through the solid and behaves as if it were a mobile positive charge. Only mobile charge carriers contribute to the conductivity; electrons paired in the valance structure are generally unavailable for conduction. Thus, the conductivity of a solid is dependent on the concentration of charge carriers. However, the rate at which the electron or hole can move in an electrical field also determines the conductivity. Thus, the measured conductivity (σ) is determined by:

$$\sigma = e (n\mu_n + P \mu_p)$$

σ = conductivity

e = electronic charge = 1.6×10^{-19} ccoulombs

* The term "hole" which refers to one net positive charge should be distinguished from "defect" or "vacancy" which imply displaced or absent atoms in the crystal.

n = number of electron carriers

P = number of holes

μ_n = mobility of electrons

μ_p = mobility of holes

Measurement of the conductivity only gives one of five variables in this equation. Techniques have been worked out to measure mobilities for more conventional semi-conductors such as germanium and silicon in order to calculate the carrier concentration. It may be possible to adapt some of these techniques to ZrO_2 corrosion film, however, it is of interest to examine the factors which affect the charge carrier concentration and hence the conductivity.

Pure defect free ZrO_2 at low temperature would have all valance electrons associated with atoms and none would be in the conduction band and available to carry current; hence, the material would be an insulator. However, as soon as an anion vacancy is introduced there will be 2 plus charges on the associated zirconium (Zr^{++}) which will not be paired. Since the crystal as a whole must be electrically neutral, there will be two electrons somewhere in the crystal to balance these 2 plus charges. It has been found that electrons associated with such defect sites have a very low activation energy (0.01 ~ 0.1 ev). At room temperature or above all such electrons would be available for conduction. Thus, the conductivity would increase as the number of anion vacancies increases. Other atoms can also affect the electron structure. For example niobium, if in a +5 state and substituted into the ZrO_2 lattice, would still have one plus charge to

contribute conductivity. Other alloy ingredients which are substituted in the ZrO_2 lattice should affect the conductivity by producing electrically active sites.

The conductivity can be affected thermally when the thermal energy is high enough to promote an electron from the immobile valance band to the mobile conduction band. This process is called "intrinsic" conduction since it is present regardless of the defect state of the material.

Radiation can also affect the conductivity since neutrons (> 1 mev) which bombard the crystal will produce both vacancies and displacement interstitial atoms, both of which produce active sites for conduction electrons.

Electrical Resistance of ZrO_2 Corrosion Films in Non-Oxidizing Atmospheres

The corrosion of zirconium alloys is generally considered to be by way of oxygen diffusion from the environment to the metal via oxygen anion vacancies. The concentration of these oxygen vacancies will be highest near the metal surface and lowest at the outer surface. This concentration gradient is schematically represented in Figure 1, Curve A. If the sample is heated in a non-oxidizing environment such as vacuum or pure helium, the zirconium-oxygen reaction will continue without a compensating influx of oxygen from the environment. This will result in a net increase in the number of oxygen vacancies in the film, with the greatest percentage increase near the outer oxide surface. This is represented schematically in Figure 1, Curve B. The increase in vacancy concentration should also produce an increase in the electron concentration available for conduction.

915-8

FIGURE 18-1 SCHEMATIC REPRESENTATION OF OXYGEN VACANCY CONCENTRATION

The electrical resistance of the corrosion film on Zircaloy-2 was measured using the resistance assembly in Figure 2. A Zircaloy-2 wire was welded to the sample to form one electrode and three graphite contacts with platinum lead wires were secured against the corrosion film. The electrical resistance between the electrodes as a function of time in high vacuum is plotted in Figure 3; in helium in Figure 4 and pure hydrogen in Figure 5. All of these curves show a similar decrease in electrical resistance with time. Resistance variations of a factor of 10^6 are observed as the atmosphere is shifted from oxidizing to non-oxidizing. If an oxidant such as H_2O or O_2 is admitted the resistance immediately begins to rise. These results are in agreement with the corrosion theory and qualitatively support the existence of oxygen anion vacancies.

The results of the hydrogen experiment in Figure 5 proved interesting because the sample did not begin to absorb hydrogen until the electrical resistance had dropped to about 50 ohms. It has been established⁽²⁾ that gas phase hydriding occurs when the oxidant supply becomes diffusion limited to the extent that the rate of supply becomes insufficient to maintain the oxidation rate normal for that temperature. Since the increase in oxygen vacancies also occurs when the oxidant supply is insufficient, this suggests that the initiation of gas phase hydriding may be related to a higher hydrogen diffusion rate made possible by the higher concentration of oxygen vacancies at the outer surface of the film.

915-7

FIGURE 18-2 ELECTRICAL RESISTANCE ASSEMBLY

FIGURE 18-3 RESISTANCE CHANGE OF ZrO_2 FILM ON ZIRCALOY-2 IN HIGH VACUUM

915-4

FIGURE 18-4 RESISTANCE CHANGE OF ZrO₂ FILM ON ZIRCALOY-2 IN HELIUM - 450°C

FIGURE 18-5 PLOT OF ELECTRICAL RESISTANCE FOR Zr-2 EXPOSED TO A GAS ENVIRONMENT AT 450°C

Variation of Electrical Resistance with Temperature

If the electrical resistance between the point contact and the base metal is plotted as $\log R$ vs $1/T$ a fairly straight line results from which an "activation energy" can be calculated. A typical plot in He-O₂ is given in Figure 6 for oxidized Zircaloy-2. The slope of this line yields an activation energy of about 11 to 17 K cal or about 1/2 ev. The thermal process being measured is, at present, not well defined, but possible contributions to such a thermal effect could be: (1) thermal variation of the oxygen vacancy concentration as a result of a thermal effect on the corrosion reaction, (2) a thermal effect on the mobility of the conduction electrons, or (3) thermal activation of electrons from the valance band to the conduction band or the so-called intrinsic conduction process. It is interesting to note that the activation energy for intrinsic conduction in a more conventional semi-conductor such as germanium is also about 1/2 ev.

Insufficient data are available at present to reach any conclusions about this activation energy but as variables such as heat treatment, alloy content or radiation effects are observed, it is a number which may provide additional information.

Corrosion Hydrogen Absorption - Heat Treatment and Electrical Resistance

At the 11th Annual AEC Corrosion Symposium in 1962, H. H. Klepfer of Valecitos Atomic Laboratories presented a paper which assembled a number of facts concerning corrosion hydrogen absorption and possible mechanisms. (3) A part of his analysis is given in Figure 7. As an oxygen

FIGURE 18-6 LOG R vs 1/T PLOT OF RESISTANCE OF ZrO_2 CORROSION FILM ON ZIRCALLOY-2

915-6

FIGURE 18-7 SCHEMATIC REPRESENTATION OF CORROSION PROCESS

ion migrates to the metal two negative charges are carried to the metal. To preserve electrical neutrality these charges can be neutralized by electron migration outwards or proton migration inwards. With this model it follows that if the electrical conductivity of the corrosion film for electrons could be increased without altering the proton mobility, the fraction of corrosion hydrogen entering the film could be reduced, alleviating a serious problem with zirconium alloys. Thus, electrical conductivity measurements could prove to be a valuable tool on which to base an alloying program.

It was reported in 1962 by S. Kass of Bettis Atomic Power Division that the beta quench heat treatment for Zircaloy-2 reduced the fraction of corrosion hydrogen absorbed.⁽⁴⁾ This result has been confirmed by H. P. Maffei of Hanford Laboratories.⁽⁵⁾ With this difference in mind the electrical resistance of the corrosion films on alpha annealed and beta quenched Zircaloy-2 and crystal bar zirconium were measured. These results are given in Table I. It can be seen that for equal corrosion film thicknesses the beta quenched Zircaloy-2 has a lower electrical resistance than the alpha annealed material. There appears to be little difference in the crystal bar zirconium except that the absolute values of the resistance are somewhat higher.

A possible explanation for this behavior would be that heating into the beta phase puts more alloying ingredients into solution. This results in a more uniform distribution of alloying ingredients in the corrosion film. Since substituted foreign atoms in the ZrO_2 lattice can form active

FIGURE 18-8 LOG R vs $1/T$ PLOT OF RESISTANCE OF ZrO_2 FILM ON ZIRCALOY-2 IN-REACTOR

decrease is attributed to the generation of radiation induced vacancies and interstitials which produce electrical charge carriers. Little temperature dependence is seen in the radiation field because the radiation induced defects are relatively constant at all temperatures and overshadow the thermal effect.

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SOLUTE DISTRIBUTION BETWEEN CORROSION FILMS
AND ZIRCONIUM ALLOY SUBSTRATES

by

✓
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INTRODUCTION

The development of oxidation-resistant alloys has been empirical for the most part due to a noticeable lack of basic theories which would permit development from a fundamental approach. The Wagner-Hauffe rules⁽¹⁻³⁾ have provided a starting point for metals which form semiconducting oxide films. The effect of alloying additions in the metal has thus been analyzed with respect to the anticipated defect structure of the oxide upon the incorporation of the alloying elements into the oxide. It is then possible to analyze the rate-controlling diffusion steps through the oxide for films of various compositions. Much of the analysis of oxidation of alloys has been done in terms of this theory, but no meaningful results can be obtained unless both the actual film composition and the diffusion rates of the proper species are known. There are no cases, to the knowledge of the author, where both of these factors are known.

Until recently, there has been no way of determining film compositions in situ. It has been necessary to physically or chemically remove the film and subsequently analyze for each constituent. This technique has been successfully employed with stainless steels,^(4,5) although in these cases the diffusion rates of the rate-controlling species have not been determined. The advent of the electron microprobe analyzer has opened up new avenues of approach to the problem of determining film composition.

The development of zirconium alloys has been restricted for the above reasons. No suitable means of film removal have been available, and no data exist in the literature on microprobe analyses of oxide films. This paper reports some preliminary work on both microprobe analyses of corrosion films and on gross chemical analysis of stripped films on the same alloys.

Another important question which has not been answered is how the film composition changes during the course of oxidation. Wagner⁽⁶⁾ has shown that solid solutions of widely differing oxidation potentials undergo preferential oxidation which will lead to compositional changes in both the oxide film and in the alloy substrate. This paper also reports the results on films of different thicknesses (corresponding to either different times at a given temperature or different temperatures for a given time) which correspond to different stages of the oxidation process.

The effect of the various alloying additions on oxygen diffusion in the oxide is being studied simultaneously, the diffusion of oxygen in the pure oxide having been reported previously by the author.⁽⁷⁾ It is anticipated that all of these studies will provide an understanding to the corrosion behavior of existing alloys and will facilitate future alloy development.

EXPERIMENTAL PROCEDURES

Alloy Preparation

Ingots were prepared by arc melting consumable electrodes of sponge zirconium, electron-beam-melted niobium, and C.P. tin. Melting was performed three times to insure homogeneity of the ingots. The ingots were canned in mild steel and extruded at 850 C. The jacketing was removed, the surface cleaned, and the alloys cold-rolled to strip with intermediate anneals at 650 C. The final strip was cut into corrosion coupons, pickled, and annealed 24 hours at 800 C and furnace-cooled.

Corrosion Tests

Triplicate samples were tested in both 360 C water and in 400 C steam in Type 347 stainless steel autoclaves. Deionized water of pH 7 was used. An argon flush was used to purge air from the autoclaves. The samples were removed intermittently, weighed, and retested for periods up to 112 days.

Film Stripping

Corrosion samples were abraded on the edges to expose the substrate metal and subjected to metal dissolution in ethyl acetate-10% bromine solutions at 74°C. The substrate was completely dissolved within one to two hours, leaving the oxide film intact in the case of thick films and in small pieces in the case of thin films. The films were then subjected to wet chemical analysis for each of the minor alloying constituents. Duplicate samples were run for each analysis; NBS standards were used as independent checks. The accuracy is given as $\pm 10\%$ of the amount analyzed.

Electron Microprobe Analysis

Some representative alloys were prepared for metallographic examination, the corrosion coupons being mounted perpendicular to the plane of section with the exception of two samples which were mounted as taper sections. The samples

were ground through 6 micron diamond dust and attack-polished with dilute HF solution with Linde A abrasive. No etch was employed. The mounts were thinned to the maximum value handled by the probe and then vapor-coated with aluminum in a coating unit employed for electron microscopy shadowing.

Microprobe traverses were performed on an ARL microprobe at both the ARL Laboratories in Glendale, California and at NM&PO (General Electric) in Cincinnati, Ohio. Continuous traverses were made at the rate of 8 microns per minute employing a multiplexing device to determine and record data from three elements in rapid succession. Suitable standards were not available, therefore no corrections were made to the data for either fluorescence or adsorption. Data will be presented in a comparative fashion; all of the samples were run under identical settings.

Electron back-scattering micrographs were made on one alloy to ascertain if gross inhomogeneities existed in the samples.

RESULTS

The corrosion behavior of all alloys studied is shown in Figure 1-2 on double logarithmic plots of weight gain versus time. Increasing amounts of either alloying addition in a given ternary system, the other alloying element remaining constant, resulted in an increased corrosion rate in 360 C water and in earlier corrosion transition. The same behavior occurred in Zr-Sn-Nb alloys in 400 C steam, but the presence of 4% chromium instead of 1% (in the presence of 2% tin) resulted in much lower corrosion rates in 400 C steam.

A summary of corrosion conditions, alloy composition, film thickness, and calculated film compositions are listed in Table I. The film analyses have been converted to atomic percents by making the assumption that the total amount of cations in the oxide are given by the stoichiometric amount of zirconium, i.e. all alloying elements substitute for zirconium in ZrO_2 . Any departures from stoichiometry with respect to anions would give a negligible change in the stated film compositions.

The chromium content of films formed on a given chromium-containing alloy was nearly the same in both the "thin" and "thick" films. Chemical analysis of chromium is perhaps the most reliable of the elements analyzed in this study, and thus good reliability is placed upon these values.

Figure 19-1. CORROSION BEHAVIOR OF Zr-Sn-Nb ALLOYS

Figure 19-2. CORROSION BEHAVIOR OF Zr-Cr-Sn AND Zr-Cr-Nb ALLOYS

TABLE I
CORROSION DATA AND CORROSION FILM COMPOSITIONS OF SOME ZIRCONIUM ALLOYS

Alloy Comp.			Corrosion Test Data					Corrosion Film Composition				
Cr	Nb	Sn	Temp. °C	Medium	Time, Days	Weight Gain mg/dm ²	Film Thickness μ	Chromium a/o	Niobium a/o	Tin a/o	Nickel a/o	Iron a/o
2	2	--	360	Water	112	128	8.5	0.70	1.01	--	--	--
2	2	--	400	Steam	105	328	22	0.72	0.82	--	--	--
1	--	2	360	Water	112	56.7	3.8	0.40	--	0.48	--	--
1	--	2	400	Steam	105	3620	240	0.40	--	0.12	--	--
4	--	2	360	Water	100	183	12	1.59	--	0.81	--	--
4	--	2	400	Steam	100	680	45	1.59	--	0.64	--	--
--	1	2	360	Water	98	67.6	4.5	--	0.26	0.29	--	--
--	1	2	400	Steam	98	302	20	--	0.28	0.26	--	--
--	2	2	360	Water	112	108	7.2	--	0.70	0.40	--	--
--	2	2	400	Steam	105	410	27	--	0.62	0.10	--	--
--	2	3	360	Water	100	138	9.1	--	0.87	0.73	--	--
--	2	3	400	Steam	100	549	36	--	0.81	0.29	--	--
Zircaloy-2			360	Water	112	36.8	2.5	0.08	--	0.20	0.45	0.20
Zircaloy-2			400	Steam	105	126	8.3	0.08	--	0.25	0.07	0.12

The niobium analyses also showed little difference between thin and thick films on a given alloy, but the reliability of niobium analysis is less than that of chromium. Duplicate and some cases triplicate samples were run on each film and were consistent throughout.

The tin analyses were the least accurate, unfortunately, and were made by dissolving the stripped films in HCl-HF solution with a cover gas of CO_2 . The acid solution dissolves the films completely and also reduces the Sn^{+4} to Sn^{+2} (if indeed the tin did exist in the stannic form). In the absence of the inert gas the oxidation of the stannous ions to the stannic form would occur and the subsequent volumetric titration of the iodine would be erroneous.

One source of error on all analyses was the small sample size, ranging from as little as 20 mg to several hundred mg. The thickest film, 230 microns, formed on the Zr-2Sn-1Cr alloy in 400 C steam, was subjected to tin analysis three times and gave values of 0.34 ± 0.03 percent. It was felt that this value was the most reliable of the tin analyses.

The significant observation from chemical analysis was that the tin concentration decreased appreciably in every case from the thin films to the thick films. If this observation is real, the implications on corrosion behavior could be significant. Much of this paper will concern the meaning of this observation and the limitations in accepting it a priori.

Microprobe traverses of two alloys are shown in Figures 3 and 4. Each figure shows a thin and thick film, formed by corrosion in 360 C water and in 400 C steam, respectively. The difference in thickness is about 4:1, and the designations of "thin" and "thick" are therefore only relative; they do not imply that the thin film region, i.e. interference color region, exists in which a logarithmic law would govern oxidation.

The traverses were made without suitable standards. Pure metals were ilable, which would be suitable for zirconium but not for the alloying elements which were present as minor additions. In order to detect differences in the minor additions it was necessary to increase instrument sensitivity which is accompanied by a large increase in the background. The large difference in absorption and fluorescence characteristics between oxide and metal would thus result in a difference in background for each element from one phase to the other.

Figure 19-3. Zr-25Sn-2Nb MICROPROBE TRAVERSES OF CORROSION SAMPLES

Figure 19-4. Zr-3Sn-2Nb MICROPROBE TRAVERSES OF CORROSION SAMPLES

Background figures were obtained by fixing the electron beam on a given spot for several minutes, resulting in rather broad bands which are shown in Figures 3 and 4.

The niobium traverses in both oxide and metal gave values which were either partially or wholly within the background band. The niobium $K \alpha_1$ line was used, the wave length of $0.746 \text{ \AA}$ being very close to $0.786 \text{ \AA}$ for zirconium $K \alpha_1$. Although these lines are far enough apart for detection, the intensity of the white radiation from the major constituent, zirconium, is of about the same intensity of the niobium $K \alpha_1$ radiation, and the detection of small differences in niobium concentration in a zirconium matrix is therefore very difficult.

The tin traverses were made with the $L \alpha_1$ line of tin of wave length $3.600 \text{ \AA}$. This value is in the low-intensity portion of the continuous white radiation of zirconium, and the peak to background ratio was sufficiently high for detection of tin variations. The variation of the tin content in the alloy is seen to vary rather widely over small distances and may be attributed to the difference in tin content between the two phases within the alloy substrate. It is not possible to correlate the variations with microstructure due to the fact that the beam diameter, 2 microns, was slightly larger than the size of the second-phase particles as seen in the microstructure in Figure 5. The beam overlapped the particles and gave a semi-integrated value.

The difference between 2 and 3 atom percent tin in the two alloys was noted for identical traverse conditions. The 2 a/o tin gave a value of 47 ± 5 units, whereas the 3 a/o tin gave a value of about 56 ± 5 units. The higher tin content of the oxide films on the Zr-3Sn-2Nb alloy compared to that of the film on the Zr-2Sn-2Nb alloy was also detectable. The tin content as detected by the microprobe did not appear to vary between the films formed at the two different temperatures for a given alloy. This result was not consistent with chemical analysis which showed a definite decrease in tin in the thick film (400 C steam corrosion).

It is thought that the chemical analyses are more reliable than the microprobe analyses due to the lack of suitable standards and the large experimental scatter. Supplementary checks were made to determine if the oscillatory

2000X

Figure 19-5. SUBSTRATE OF Zr-2Sn-2Nb

variations in the probe analyses were real or due to experimental scatter. The thickest film available, Zr-2Sn-1Cr corroded 105 days in 400 C steam, was examined by fixing the electron beam on a given point and noting the intensity band obtained over a duration of several minutes. Some areas examined definitely showed chromium-rich regions, although the enrichment was not large. It may thus be concluded that the oxide films were not completely homogeneous, although it is not possible to determine what the concentration fluctuations are. There does not appear to be a concentration gradient of any of the elements through the film, although the inhomogeneities exist at both the outer and inner portions.

The nature of the oxide films which were traversed by the electron microprobe is shown in Figure 6. The samples were polished through 6 micron diamond dust and then attack polished in a dilute solution of HF using Linde A abrasive.

Prior to metallography, all samples were flashed with metallic silver in a silver nitrate solution followed by copper plating. The plating was performed to preserve the edges during grinding and polishing, and the silver flash was performed to increase the throwing power of the copper during plating. The copper plating also served to fill pre-existing cracks with copper which permitted identification of these cracks with respect to those which formed during grinding, etc.

Most of the films appear to be free of substructure, although the Zr-2Nb-2Sn alloys have what may be either second phase particles or pulled-out portions. Microprobe results did not indicate the presence of any massive second phases; slight inhomogeneities did exist as mentioned already.

The thickest oxide film, formed on Zr-2Sn-1Cr in 400 C steam, is also shown in polarized light. There are numerous cracks parallel to the surface and a lesser number of cracks normal to the surface. The parallel cracks would provide a diffusion barrier during oxidation, lateral diffusion being required to circumvent the cracks.

Electron micrographs of replicas made directly from the corrosion sample surface are also given, as shown in Figure 7. In several cases cracks may be observed and a ridge existed on the replicas which was indicative of "valleys" on the sample surface.

DISCUSSION

The best basis of comparison of oxide film compositions is obtained by using the atom ratios of zirconium to each alloying constituent in order to account for the dilution effect of oxygen in the oxide. Table II lists the atomic ratios for both alloy substrates and oxide films. It may be seen that the Zr/Cr ratio in Zr-2Cr-2Nb films has remained nearly the same as in the metal and does not vary from the thin to thick film. The Zr/Nb ratio in the film decreased somewhat from its original value in the metal and once again did not vary too greatly from the thin to thick films, although more so than for the Zr/Cr ratio. The film composition of this alloy does not appear to change during the course of oxidation.

The Zr-2Sn-1Cr alloy showed a slight decrease (97 to about 81-82) for the Zr/Cr ratio, but the Zr/Sn ratio for both thin and thick films was greater in the film than in the alloy. The thick film contained much less tin than the thin film as indicated by the increase in Zr/Sn ratio from 67.7 to 274. The low ratio (higher tin content) is associated with better corrosion resistance than the high ratio. An increase in the chromium content to 4 a/o, tin remaining at 2 a/o, resulted once again in nearly identical Zr/Cr ratios in both thin and thick films, the values being slightly less than in the alloy. However, unlike the alloy containing 1 a/o chromium, the Zr/Sn ratio was close to the original value and not too different between thin and thick films. This alloy exhibited significantly better corrosion resistance than the low-chromium alloy. The increased corrosion resistance correlating with the higher tin content of the oxide film.

The two Zr-Nb-Sn alloys for which values are given in Table II showed very little change in Zr/Nb ratio from alloy to oxide and from thin to thick films. Once again, it may be noted that the Zr/Sn ratios were noticeably higher in the oxide than in the metal and higher in the thick film by a factor of about 3-4 compared to the thin films. In these cases the correlation with corrosion resistance is not too clear. The alloy containing 3 a/o tin corroded more rapidly than the alloy containing 2 a/o tin, but in contrast to the Zr-Sn-Cr alloys the tin content of the oxide film of the more corrosion resistant alloy was lower than for the less corrosion resistant alloy.

112 Days 360°C

500X

105 Days 400°C

500X

Zr-2Nb-2Sn

100 Days 360°C

500X

100 Days 400°C

500X

Zr-2Nb-3Sn

112 Days 360°C

500X

Taper Section, 45°

105 Days 400°C

150X

Zr-2Sn-1Cr,

Figure 19-6. CORROSION FILMS OF SOME TERNARY ZIRCONIUM ALLOYS

Figure 19-6. CORROSION FILMS OF SOME
TERNARY ZIRCONIUM ALLOYS (Continued)

98 Days 360°C

2000X

98 Days 400°C

2000X

Zr-1Nb-2Sn

100 Days 360°C

2000X

100 Days 400°C

2000X

Zr-2Nb-3Sn

112 Days 360°C

2000X

Zr-2Sn-1Cr

Figure 19-7. ELECTRON MICROGRAPHS OF OXIDE FILM SURFACES

TABLE II

ATOMIC RATIOS OF SOLVENT TO ALLOY ADDITIONS
IN SUBSTRATES AND CORROSION FILMS

Alloy	Atom Ratios			Film Thickness Microns	Oxide Film Atom Ratios		
	Zr/Cr	Zr/Sn	Zr/Nb		Zr/Cr	Zr/Sn	Zr/Nb
2Cr-2Nb	48.0	--	48.0	8.5	45.5	--	31.8
2Cr-2Nb	48.0	--	48.0	22	44.4	--	39.0
1Cr-2Sn	97.0	48.5	--	3.8	81.0	67.7	--
1Cr-2Sn	97.0	48.5	--	240	82.3	274	--
4Cr-2Sn	23.5	47.0	--	12	19.7	38.6	--
4Cr-2Sn	23.5	47.0	--	45	19.8	49.2	--
2Nb-2Sn	--	48.0	48.0	7.2	--	80.3	46.0
2Nb-2Sn	--	48.0	48.0	27	--	326	51.8
2Nb-3Sn	--	31.7	47.5	9.1	--	43.3	36.3
2Nb-3Sn	--	31.7	47.5	36	--	111	39.7

Application of film composition data to the Wagner-Hauffe oxidation rules can be performed only for cases in which a diffusion-controlled process governs oxidation. The alloys in this study all exhibited linear corrosion kinetics for the corrosion times involved, and a rigorous analysis of the oxide film defect structures would therefore have no meaning. In order to make the necessary analysis of the data it would be necessary to examine alloys which had not undergone transition from parabolic (or cubic) to linear kinetics. Unfortunately, the weight gains for transition are very low, about 20-40 mg/dm², and correspond to very thin films of less than 2 microns. The amount of sample which could be stripped for chemical analysis would be in the milligram range even if considerable sample area were involved. The thin films would also provide experimental difficulties for microprobe analysis in view of the minimum beam diameter of about 2 microns. Taper sections would magnify the film thickness, but the beam would then penetrate the outer edge completely.

Generally speaking, it is not possible to obtain thick films on zirconium alloys which have formed a parabolic rate law. Further, most metallic elements are relatively insoluble in alpha zirconium (with the exception of titanium and hafnium), and it is thus difficult to interpret the compositional changes of oxide films by virtue of selective oxidation.

Wagner⁽⁶⁾ has shown both theoretically and experimentally that Ni-Pt alloys oxidize to form NiO, the platinum remaining unoxidized. A concentration gradient will then exist in the substrate adjacent to the metal-oxide interface which is enriched in platinum and depleted in nickel. Continued formation of nickel oxide is then dependent upon a supply of nickel atoms which must diffuse from the interior of the alloy. The same behavior could occur in Zr alloys containing tin, in which the oxidation of zirconium would occur much more readily than for tin. Although some tin would be oxidized, it would not be unreasonable to expect a concentration gradient of tin in the substrate adjacent to the oxide film. There was no evidence from microprobe analyses of tin enrichment at the interface; however, the large experimental scatter may have masked the effect.

Selective oxidation of soluble constituent such as tin would result in a continuous change in the oxide film composition. There should be no effect on oxidation kinetics if tin existed in the oxide as Sn⁺⁴, but if tin were present

as Sn^{+2} , a significant increase in anion vacancy concentration would occur giving rise to more rapid oxygen ion diffusion and corrosion.

There are no data available in the literature which indicates the solubility limits of the cations of interest in zirconia. The formation of second phases within the oxide layer would completely change the analysis of the oxidation behavior. In addition to solubility limits, there is a need to learn the valence of each cation in the oxide. Elements such as chromium and niobium are polyvalent and could either improve or harm oxidation resistance, depending upon their valence in the oxide.

CONCLUSIONS

Preliminary data have been given for oxide film composition on several ternary zirconium alloys. The atom ratio of Zr/beta-stabilizing solute does not change appreciably from substrate to oxide and from thin to thick films. The ratio of Zr/Sn does change significantly, increasing from substrate to film and increasing from thin to thick films. The latter behavior may be due to selective oxidation of tin, the only element studied having appreciable solid solubility in alpha zirconium, although no concentration gradients of tin in the substrate were detected by microprobe analyses. The failure to detect a gradient may be due to experimental shortcomings of the analysis which are described in detail.

Although significant changes in concentration of tin appear to exist from alloy to alloy and from thin to thick films, it is not possible to apply the Wagner-Hauffe rules inasmuch as the alloys were corroding according to a linear rate law. The study indicates the type of measurements needed to make a rigorous analysis of oxidation behavior and serves to point out limitations of the various methods.

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NOTE ON THE DEFECT STRUCTURE OF ZrO_2 AND HfO_2

by

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ABSTRACT

The defect structure of ZrO_2 and HfO_2 has been studied through measurements of electrical conductivity as a function of oxygen pressure. The electrical conductivity exhibits an unusual and complex oxygen pressure dependence, and to explain the results it has been proposed that these oxides are ionic conductors, and that a "coupled" transport of oxygen vacancies and interstitials is faster than an independent transport of these defects.

Thermogravimetric measurements on ZrO_2 suggest that the non-stoichiometry of this oxide is more than a factor of ten smaller than that observed by Aronson⁷⁾.

NOTE ON THE DEFECT STRUCTURE OF ZrO_2 AND HfO_2

INTRODUCTION

The oxidation mechanism of zirconium is not well understood. This is partly due to a lack of knowledge of the relative importance of and interplay between oxygen dissolution in the metal and oxide (ZrO_2) formation¹⁾. From various studies¹⁻⁹⁾ it is reasonable to conclude that the ZrO_2 -layer has a protective effect and that a transport of ions through the scale at least partially determines the rate of oxidation of zirconium.

The elucidation of the oxidation mechanism of a metal forming a protective oxide scale, of course, requires knowledge of the defect structure of the oxide. In interpretations of the oxidation mechanism of zirconium the defect structure of ZrO_2 is commonly assumed to involve oxygen vacancies and a corresponding n-type conductivity⁴⁻⁹⁾. However, studies by Rudolph¹⁰⁾ have shown that the electrical conductivity of ZrO_2 is proportional to about $p\text{O}_2^{1/5.2}$ at 900-1000°C in the oxygen pressure range 760 to 0.1 torr. This may suggest that ZrO_2 is a p-type conductor under these conditions.

Although a large number of studies of oxidation of zirconium and zirconium alloys and corresponding attempts to elucidate the oxidation mechanism have been carried out, relatively little effort has been made to obtain a good working knowledge of the defect structure of ZrO_2 . The present work is an attempt in this respect by measuring the electrical conductivity as a function of oxygen pressure. Studies on HfO_2 have also been included as this oxide closely resembles ZrO_2 . In addition, attempts to make thermogravimetric measurements of the defect structures of these oxides have been made.

MATERIALS AND METHODS

Spectrographically standardized ZrO_2 powder was obtained from Johnson, Matthey & Co. Ltd. According to the suppliers, estimates of impurities are as follows: Hf - 1.7 %; Si - 5 ppm; Na - 1 ppm; and Cu and Mg - < 1 ppm.

HfO_2 powder was supplied by the Wah Chang Corp., and estimates of impurities contents are: Zr - < 1000 ppm; Fe - < 100 ppm; W - < 50 ppm; Si - 50 ppm; Cu - < 40 ppm; Al - < 25 ppm; Ti - < 20 ppm; Cr, Mg, Mn, Mo, Ni, and Sn - < 10 ppm; Pb, Co, and V - < 5 ppm; and Cd - < 1 ppm.

Specimens were prepared by sintering cold-pressed powders in air at 1400°C .

In the studies of electrical conductivity two Pt-10 % Rh plates served as electrodes, and these were pressed against the ends of the specimens by a spring-loading method. The resistance was measured with a Wheatstone bridge using direct current. The ZrO_2 -specimen had a cylindrical shape with a diameter of 1.70 cm and a height of 1.65 cm. The density was 4.70 g/cm^3 . The HfO_2 -specimen had a diameter of 2.1 cm. The density was 5.80 g/cm^3 .

Measurements of the electrical conductivity as a function of oxygen pressure were made in pure oxygen gas at different pressures, in mixtures of argon and oxygen, and in mixtures of $\text{CO} + \text{CO}_2$ to obtain low partial pressures of oxygen¹¹⁾. The equilibration periods varied from 1/2 hr to 1 day depending on the temperature.

The thermogravimetric measurements were carried out in a quartz helix type apparatus¹²⁾. The weight of the oxide was measured in O_2 , in mixtures of $\text{CO} + \text{CO}_2$, and in pure CO. All measurements were made at a total gas pressure of 1 atm. Particular care was taken to avoid buoyancy due to thermomolecular or radiometer effects, which may cause serious errors in thermogravimetric measurements¹²⁾.

RESULTS AND DISCUSSION

Electrical conductivity studies

In the measurements of electrical conductivity of ZrO_2 hysteresis of the monoclinic-tetragonal transformation was observed. This is shown in Fig. 1, where the resistance of the specimen is plotted as a function of decreasing and increasing temperatures at a constant partial pressure of 0.009 atm. The measurements in Fig. 1 were taken at rapid heating and cooling ($\sim 3^\circ \text{C/min}$), but essentially the same curve was obtained by equilibrating the specimen for about 24 hrs. at each temperature. At increasing temperature the transition was very rapid and occurred at $1200\text{--}1205^\circ \text{C}$, while at decreasing temperature the transition was more sluggish and took place at $1000\text{--}1050^\circ \text{C}$. The observed transition temperature of 1200°C is in good agreement with recent studies of this phase transformation^{13, 14}.

The results of the studies of conductance of the ZrO_2 and HfO_2 specimens as a function of oxygen pressure are shown in Figs. 2 and 3, respectively. During measurements the system was kept at constant temperature. In order to avoid hysteresis effects associated with the ZrO_2 phase transformation, the results in Fig. 2 only include measurements taken under a sequence of increasing temperature.

If one expresses the conductance of the specimen as

$$\sigma = \text{const. } p_{\text{O}_2}^{1/n} \quad (1)$$

it is seen that for HfO_2 n has negative values at oxygen pressures above $10^{-3}\text{--}10^{-4}$ atm. At $800\text{--}900^\circ \text{C}$ and close to 1 atm. O_2 n has a value of about -4, while at higher temperatures the value of n becomes larger. At $10^{-3}\text{--}10^{-4}$ atm. O_2 the conductance goes through a maximum and then decreases with decreasing oxygen pressure. Below $10^{-6}\text{--}10^{-8}$ atm. O_2 the conductance becomes approximately independent of oxygen pressure.

FIG. 20-1. The resistance of the ZrO_2 specimen as a function of increasing and decreasing temperature at a partial pressure of oxygen of 0.009 atm.

FIG. 20-2. The conductance of the ZrO_2 specimen as a function of the partial pressure of oxygen.

FIG. 20-3. The conductance of the HfO_2 specimen as a function of the partial pressure of oxygen.

ZrO₂ shows the same general type of behaviour. For tetragonal ZrO₂ n has negative values close to 1 atm. O₂. The conductance goes through a slight maximum at about 10⁻³ atm. O₂ and goes through a minimum at about 10⁻⁶-10⁻⁷ atm. O₂. Below this pressure n takes on negative values.

For monoclinic ZrO₂ n has in general positive values above 10⁻⁸-10⁻⁹, but the conductance becomes less oxygen pressure dependent with increasing oxygen pressure. The results also suggest a slight maximum at 10⁻² atm. at 927 and 977° C, similar to the maximum observed for HfO₂. Below 10⁻⁸-10⁻⁹ atm. O₂ n again takes on negative values.

Compared with other oxide semiconductors the conductivity of HfO₂ and ZrO₂ shows a very complex oxygen pressure dependence. This is indicative of a complex defect structure and interrelated effects of charge carrier mobilities.

Ionic defects which concentrations are dependent on the oxygen pressure, include oxygen and cation vacancies and interstitials. Oxygen defects may be described by the equations

where $O_1^{\bar{}}$ designates an oxygen ion in a normal lattice position, Ov an oxygen vacancy, O_i an oxygen interstitial, e^{-} an electron in the conduction band, and e^{+} an electron hole. p and q may have values from 0 to 2. In addition one should also consider intrinsic ionization in the oxides. This may be written as

A qualitative consideration of these defect equilibria gives the following limiting conditions:

- 1) If intrinsic ionization (Eq. 4) predominates, the electrical conductivity is independent of oxygen pressure and the concentration of electrons (or electron holes) is given by

$$[e^-] = K_4^{1/2} \quad (5)$$

- 2) If intrinsic ionization is negligible, the electrical conductivity is determined by Eqs. 2 and 3:

- a) At very high pressures Eq. 3 will predominate and the defect equilibrium will essentially be given by

$$[O_i^{-q}] [e^+]^q = K_3 p_{O_2}^{1/2} \quad (6)$$

Under these conditions both the concentration of electron holes and interstitial oxygen ions will be proportional to $p_{O_2}^{+2(1/q+1)}$.

- b) At very low pressures Eq. 2 will predominate and the defect equilibrium will essentially be given by

$$[O_v^{+p}] [e^-]^p = K_2 p_{O_2}^{-1/2} \quad (7)$$

Under these conditions both the concentrations of electrons and of oxygen vacancies will be proportional to $p_{O_2}^{-1/2(p+1)}$.

On the basis of the above defect structure model one would thus expect that the electrical conductivity is proportional to $p_{O_2}^{1/2(q+1)}$ at very high oxygen pressures and proportional to $p_{O_2}^{-1/2(p+1)}$ at very low oxygen pressures. At the transition from p- to n-type conductivity one would also expect a minimum in conductivity. A defect structure of this type has been proposed for Ta_2O_5 ¹⁵⁾.

A corresponding analysis of a defect structure involving cation vacancies and interstitials would lead to the same general conclusions, i.e. one would expect p-type conductivity at high oxygen pressures and n-type at low oxygen pressures. Similarly a minimum in the conductivity versus p_{O_2} curves would be expected at the p-n transition. The same oxygen pressure dependence would be expected regardless of whether one has predominant electronic conduction or a predominant ionic conduction with independent migration of the defects.

As seen in Fig. 3 the conductivity of HfO_2 shows a maximum at 10^{-3} - 10^{-4} atm. O_2 and with an apparent n-type conductivity at higher oxygen pressures and p-type at lower oxygen pressures. This experimentally observed pressure dependence is thus the opposite of the behaviour discussed above. Therefore it does not appear possible to the authors to explain the observed behaviour in terms of predominant electronic conduction or predominant ionic conduction with independent migration of the defects or in terms of a combination of such transport processes. A possible interpretation of the results may, however, be made by assuming that ionic conduction takes place through a "coupled" transport of vacancies and interstitial ions.

If one assumes that HfO_2 and ZrO_2 has an anti-Frenkel defect structure, i.e. oxygen vacancies and interstitials, the defect structure is described by Eqs. 2-4. The concentration of oxygen vacancies will increase with decreasing oxygen pressure, while the concentration of oxygen interstitial ions will increase with increasing oxygen pressure. However, Eq. 3 will not be applicable up to extremely large oxygen pressures as this would imply an unlimited solubility of interstitial oxygen ions. One must assume that the solubility of interstitial oxygen ions approaches a limiting value with increasing oxygen pressure. The valence of the interstitial oxygen ion, i.e. the value of q , may vary from 0 to 2. Considering the size of an oxygen ion, small values of q would be favoured.

The concentration of oxygen vacancies and interstitial ions will be a very complex function of oxygen pressure and will depend on the value

of q , p , K_2 , K_3 , and K_4 : The exact relationship may be evaluated by applying the condition of electroneutrality and the law of mass action to Eqs. 2, 3, and 4^{12, 15}).

A qualitative graphical representation of the concentrations of oxygen vacancies and interstitial ions is shown in Fig. 4. In drawing the curves it is assumed that $q < p$ and that the concentration of interstitial oxygen ions approaches a solubility limit.

As discussed above an independent transport of defects will under no circumstances result in a maximum in the electrical conductivity as a function of oxygen pressure. However, if one assumes that 'coupled' or simultaneous transport of the defects is much faster than the independent migration, the electrical conductivity will be given by the product of the defect concentrations, thus $O_i^{-q} O_v^{+p}$. This product is shown as the fully drawn line in Fig. 4 and, as seen, such a mechanism may result in a maximum in the conductivity curve.

At higher and lower pressures than that of the maximum, the conductivity will decrease with pressure, until the total conductivity will be determined by another transport process or by intrinsic ionization. For HfO_2 it is proposed that when the conductivity due to the coupled transport becomes too small, the conductivity due to intrinsic ionization will predominate and the conductivity will become essentially independent of oxygen pressure (Eq. 5). This behaviour is observed for HfO_2 at $p_{O_2} < 10^{-6} - 10^{-8}$ atm. According to this model one would also expect that the conductivity becomes independent of oxygen pressure and that it is determined by the intrinsic ionization at very high oxygen pressures. The total conductivity on the basis of this model will be as shown in Fig. 4.

The same general interpretation is also proposed for ZrO_2 . For the monoclinic phase a maximum in the conductivity is suggested only at the lower temperature. Compared to HfO_2 it thus appears that the maxima are displaced towards higher oxygen pressures for monoclinic ZrO_2 .

FIG. 20-4. Proposed model for variations in defect concentrations with partial pressure of oxygen.

At $p_{O_2} < 10^{-8} - 10^{-10}$ atm. ZrO_2 exhibits increased conductivity with decreasing oxygen pressure. This may qualitatively be explained by effects of independent migration of oxygen vacancies. From Eqs. 2, 3 and 4 it is obvious that at sufficiently low oxygen pressures the oxygen vacancy defect equilibrium (Eq. 2) will eventually predominate, and if the mobility of oxygen vacancies is larger than that of the electrons, the conductivity will be given by that of the oxygen vacancies.

Due to the complexity of the defect equilibria and the transport processes, the above discussion is at present stage necessarily qualitative in nature. The observed temperature dependence and activation energies also are composites and reflect the relative importance of the defect equilibria and the mobilities of the charge carriers. Furthermore the different equilibria will most likely have different "activation energies" and the oxygen pressure dependence of the conductivity will therefore show variations with temperature.

Thermogravimetric studies

The non-stoichiometry of ZrO_2 as a function of oxygen pressure at 900-1100° C has been studied by Aronson⁷⁾. These results suggest that the non-stoichiometry (i.e. the concentration of defects) increase with decreasing temperature. Thermodynamically this is extremely unlikely. It was therefore considered worthwhile to attempt to reproduce the results of Aronson by means of thermogravimetric measurements in the same manner as for Nb_2O_5 ¹²⁾ and TiO_2 ¹⁶⁾.

Thermogravimetric measurements were made at 1100-1300° C by measuring the weight change of ZrO_2 and HfO_2 specimens when successively equilibrating the specimens in 1 atm. O_2 in mixtures of $CO + CO_2$ (p_{O_2} ranging from 10^{-7} to 10^{-18} depending on temperature), and in pure CO . Equilibration periods up to 1 day were used.

In all cases very small weight changes were observed, and in most cases the weight changes were within the limits of error of the

measurements. Because of these small weight changes it was impossible to evaluate the oxygen pressure dependence of the non-stoichiometry.

If the formula of the oxide is written as ZrO_{2-z} , the results suggest that the maximum weight loss in going from a partial pressure of oxygen of 1 to 10^{-15} atm. at 1175°C corresponds to a value of $z < 0.001$. This value suggests a non-stoichiometry which is more than a factor of 10 smaller than that observed by Aronson at $900-1100^\circ\text{C}$ ⁷⁾.

SUMMARY AND GENERAL CONSIDERATION

In the above interpretation it has been proposed that the defect structures of ZrO_2 and HfO_2 involve oxygen vacancies and interstitials. The formula of the oxides should correspondingly be written MeO_{2-x+y} , where x represents oxygen vacancies and y interstitial oxygen.

In order to explain the oxygen pressure dependence of the conductivity it has been found that the oxides are ionic conductors and that a "coupled" transport of oxygen vacancies and interstitial ions is faster than an independent transport of these defects.

In order to confirm the proposed mechanism it would be highly desirable to study the relative importance of ionic and electronic conduction as a function of the partial pressure of oxygen. In this connection it is important to note that ZrO_2 highly doped with Ca is essentially an ionic conductor involving the transport of oxygen via oxygen vacancies¹⁷⁾.

The proposed mechanism and defect structure is of importance as regards the elucidation of the mechanism of oxidation of these metals. In this respect it is also particularly important to ascertain the

relative importance of ionic and electronic conduction.

A remark should also be made with regard to the use of the Wagner-Hauffe semiconductor approach to alloy oxidation in attempts to improve oxidation resistance of metals. This approach has frequently been applied in recent years, but it has been seemingly unsuccessful in disappointingly many cases. The above discussion emphasized that a firm knowledge of the defect structure and transport mechanism in oxides is necessary before attempts to apply the semiconductor approach is made. All in all, in order to obtain a more fundamental understanding of protective oxidation of metals and alloys, more emphasis should be placed on studies of diffusion, defect structures and electrical conductivity in pure and doped oxides.

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PRELIMINARY EXPERIMENTS ON THE USE OF AC
POLAROGRAPHY TECHNIQUES IN THE DETERMINATION OF
HYDROGEN TRANSPORT MECHANISMS IN ZIRCONIUM ALLOY OXIDE FILMS

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I. INTRODUCTION

The long term integrity of zirconium base alloy structural members exposed to high purity, high temperature water is not so much in jeopardy from the degree of oxidation (which leads to a loss of member strength due to thinning as a result of conversion to ZrO_2) as it is from the absorption of hydrogen that is generated as a product of the water - zirconium alloy oxidation reaction.

The mechanism of hydrogen uptake by zirconium alloys and accompanying efforts to define alloying principles that will minimize such uptake are the subject of extensive research and development activity (1, 2). A tool in the former field that has not been extensively applied to the specific problem of hydrogen transport in ZrO_2 is a modification of ac polarography. In support of APED's program to optimize the use of zirconium base alloys in its nuclear reactors, a study, sponsored by The General Electric Company's Atomic Power Equipment Department (APED), was conceived in which ac polarographic techniques would be used in an attempt to characterize conduction in ZrO_2 films with the hope that the electronic and ionic (in particular the proton) contribution could be separated. This discussion considers the results of scoping experiments in this study.

II. EXPERIMENTAL

Annealed panel specimens of zirconium (in ppm: 875 Fe, 114 Cr, 20 Sn, 20 Ni, 11 H_2 , 32 N_2) and of a zirconium-tin alloy, Zircaloy-2 (in %: 1.33 Sn, 0.18 Fe, 0.11 Cr, 0.05 Ni, in ppm: 18 H_2 , 24 N_2), were pickled by standard procedures. They were then filmed by anodizing in 1 N H_2SO_4 to given forming voltages at constant current (0.5 mA cm^{-2}). A few specimens were also filmed by exposure to 1500 psi high purity steam at 400°C and at 440°C .

These specimens were then subjected to a series of impedance and conductivity measurements as described in the following paragraphs.

III. RESULTS AND DISCUSSION

A. Impedance Measurements

Zirconium alloy oxide films broadly fall into the semi-conductor oxide class and as such, both their capacitive and resistive components are of interest. The electrolytic cell in which these impedance, (RC), measurements were made is shown in Figure 1. Both the capacity and the resistance of the experimental ZrO_2 films were determined as a function of frequency over a range of 0.05 to 640 kcs, in 1N H_2SO_4 (the higher frequencies being obtained with a Hewlett Packard model 200 D audio oscillator). The results supported the expected linear dependence of $1/C$ vs log frequency and R vs $1/F$. However, the ratio of the slopes was not 9.2, which might be expected, particularly in the case of the anodically formed films (3). The linear dependence of the resistance on reciprocal frequency failed at the higher frequencies (>100 kcs), as has been found in other oxide systems (4). Because of this failure the film-electrolyte resistance was assumed to be that as determined at 100 kc (Table I). In most cases there was very little change in film capacitance (Table II) over a wide range of frequencies. Of particular interest, however, was the fact that the impedance bridge system used (G.R. #1650-A) allows, through dissipation factor measurements, an estimate of the connective nature of the RC component. Here, as in the interpretation of the conductivity measurements that follow, and as has been suggested by similar studies (5, 6, 7), the major resistive-capacitive connection is indicated as

FIG. 21-1. TEST CELL

TABLE I

Cell Resistance, Ω , (Determined After 18-24 Hours of Immersion) As a
Function of Frequency For Various Working Electrodes In $\text{I N H}_2\text{SO}_4$

Frequency K c/s	Working Electrode												
	Smooth Platinum	Zircaloy-2						Zirconium					
		Anodically Formed Oxides				Steam Grown Oxides (1500 psi)				Anodically Formed Oxides			
		7.4 V 293 A°	20 V 653 A°	52 V 1745 A°	152 V 5156 A°	14 Days 400°C 22480 A°	140 Days 400°C 100357 A°	2 Days 440°C 12489 A°	4 Days 440°C 17789 A°	20 V 529 A°	52 V 1377 A°	130 V 3081 A°	
2.5	14	70	160	395	1350	5800	19500	3200	4800	150	420	940	
5	10	36	80	218	680	3200	11200	2150	3000	84	240	510	
10	8	18	40	110	380	1600	6200	1160	1600	42	104	250	
25	7	12	17	40	140	690	3000	580	740	18	44	104	
50	6.5	10	13	22	90	370	1800	360	420	13	24	57	
100	7.5	10	10	14	50	195	1000	160	220	10	14	28	
250	10	12	12	12	35	86	460	75	105	14	16	18	
500	16	18	16.5	17	44	62	280	60	72	22	24	24	
640	-	-	-	-	-	62	270	-	72	-	-	-	

TABLE 11

Cell Capacitance⁽¹⁾, mμ farads (Determined After 18-24 Hours of Immersion),
As a Function of Frequency For Various Working Electrodes in 1 N H₂SO₄

Frequency CPS	Working Electrode											
	Smooth Platinum	Zircaloy-2								Zirconium Anodically Formed Oxides		
		Anodically Formed Oxides				Steam Grown Oxides (1500 psi)						
		7.4 V 293 A°	20 V 653 A°	52 V 1745 A°	152 V 5156 A°	14 Days 400°C 22480 A°	140 Days 400°C 100357 A°	2 Days 440°C 12489 A°	4 Days 440°C 17789 A°	20 V 529 A°	52 V 1377 A°	130 V 3081 A°
100	11300	950	430	160	57	16.1	3.6	21.5	-	420	158	75
300 ⁽²⁾	11100	970	435	166	57	15.4	3.35	27.5	21.5	405	160	71.5
500	10300	950	430	163	56.5	14.1	3.05	25.5	20	395	157	70
700	10000	950	430	162	55	13.3	2.95	23.2	17.3	395	153	68.5
1000	9500	960	430	161	54.5	12.5	2.80	22.5	15.8	395	151	67.5
10 ⁴	6700	900	430	151	53.5	10.5	2.25	14.8	12.8	255	143	63.5
10 ⁵	6700	890	124	122	26.7	8.3	1.84	12	4.2	40	103	43

(1) The impedance bridge will measure two basic capacitive circuits: one, series: , the other parallel . Response of the detector (in this work a voltage null on a cathode ray oscilloscope), to dissipation factor (DQ) measurements will broadly indicate which circuit should be measured. Generally, for the films herein examined, the series circuit was the more appropriate.

(2) Generally, poor detector nulls existed for frequencies below 300 cps.

being in series rather than in parallel, except for steam grown films, as will be discussed shortly. Measurements with smooth platinum as the working electrode gave a cell double layer capacity of 10 μ farads and an electrolyte resistance of 7.5 ohms.

B. Film Formation

1. Steam at 1500 psi

The kinetics of film growth in 400°C and at 440°C were comparable to those generally reported (8) for Zircaloy-2 (no zirconium was steam treated for the experiments in this discussion). Weight gain data, for the few specimens examined, are listed in Table III, with film thicknesses listed as estimated by both capacitance measurements, and by ZrO_2 density assumptions.

Film thickness can be estimated from capacity measurements from the following relationship (9), in which the major sources of error are a lack of precision in dielectric constant values, and film defects, notably crack net works:

$$l = E A \times 10^{+3} / 113 C$$

where: l = Film thickness, A°

C = Capacitance, μ farads

A = True surface area, cm^2

E = Dielectric constant

According to Wanklyn (7), A is about 1.5 greater than the geometrically measured surface area. 27 has previously been proposed the dielectric constant (10) for ZrO_2 grown on Zircaloy-2, and this number was used throughout this work in calculating Zircaloy-2 film thicknesses from capacitance measurements. It is interesting

TABLE III

Steam (1500 psi) Grown Film Data
For Zircaloy 2

Temperature °C	Exposure Time, days	Weight Gain ⁻² mg-dm	Film Thickness, ^μ m	
			By Capacity	By Wt. Gain - ZrO ₂ Density ⁽¹⁾
400	14	37.4	2.25	2.52
	140	111.2	10.00	7.50
440	2	27.2	1.25	1.87
	4	33.1	1.78	2.23

(1) Taken at 5.7 g cm⁻³

to note that the steam grown film capacities do not, here, reach the limits, as a result of extensive cracking, found by Wanklyn (8). All filmed specimens were soaked in the measuring electrolyte for 18-24 hours before impedance measurements were taken. In the case of the thick steam grown films this "conditioning" period may not have been long enough for any crack net work to become filled with the electrolyte.

2. Anodization in H_2SO_4

Zirconium and Zircaloy-2 were anodized to the forming voltages shown in Figure 2, in which film thicknesses were determined from capacity measurements using 20 as the dielectric constant for zirconium*. The slopes of the film thickness-forming voltage curves fall roughly within A°/V ranges determined in other zirconium anodization experiments (10, 12, 13).

The voltage change as a function of time during filming was similar to those shown in Figure 3. The plateau's are proportional to the oxygen evolution potential. The voltage plotted is the iR drop across both electrodes, which accounts in part for the fact that O_2 evolution was observed at 4 volts (rather than at 1.2 - 2 volts, as would be expected with a similar anodizing geometry referenced to the hydrogen electrode). Massive oxygen evolution generally occurred at between 50-60 volts on those specimens formed to the higher voltages. Formation efficiencies were low, $< 10\%$ coulombic utilization, in all anodized specimens.

*A value suggested by Charlesby and Polling, and not disputed by Misch, refs cited. However, Adams, Van Rysselberghe and Willis (11), find it to be closer to 25.

FIG. 21-2. THICKNESS - FORMING VOLTAGE RELATIONSHIP FOR ZIRCONIUM AND ZIRCALOY-2. THICKNESS DETERMINED BY CAPACITY MEASUREMENTS, WITH DIELECTRIC CONSTANTS TAKEN TO BE 27 FOR ZIRCALOY-2 AND 20 FOR ZIRCONIUM.

FIG. 21-3. FORMING VOLTAGE - TIME RELATIONSHIP FOR ZrO_2 GROWN ANODICALLY IN H_2SO_4 :

A: TO 20V FROM ZIRCALOY-2 AT $0.5 \text{ in } A/cm^2$

B: TO 130V FROM ZIRCONIUM AT $2.0 \text{ in } A/cm^2$

2. Conductivity Measurements

1. Method

The cell, Figure 1, was connected, through the circuit shown in Figure 4, to a Hewlett Packard Model 202A low frequency function generator (0.008 to 1200 cps). Voltage-time changes, at an ac, triangular wave, signal of 0.1 cps were recorded with a Dumont-Polaroid camera attachment mounted on a Tektronic #535 cathode ray oscilloscope. This instrument was also used to measure all voltages in determining the previously mentioned film resistances and was used as the null detector in determining film capacities.

The voltage, V_c , across the cell leg of the circuit was varied through the voltage divider R_2 . The current flowing from the power supply was measured across R_0 , and that flowing through the cell was measured across R_3 . The power supply voltage output was maintained constant at about its maximum of 18 volts (maximum for this particular circuit-cell geometry).

2. Results and Discussion

a. General

Two signals were used: full ac, and ac 1/2 wave rectified (anodic cycle on the working electrode suppressed). The full ac signal was employed primarily to assess the efficiency of the rectification nature of the ZrO_2 films. No quantitative efforts were made in these initial studies to relate ac response to cell parameters in as thorough a manner as discussed by Delahay (14) and Remick (15).

The anodic cycle repression through 1/2 rectification of the ac signal resulted in cyclic cathodic pulsing of the working electrode*. Numerous cathodic pulse measurements were made in the hope that should free protons H^+ , or hydrated protons H_3O^+ , be present in the oxide film they would make a detectable contribution to the conduction response. Unfortunately, the test circuit would not give the field strengths ($>10^{+6}$ V cm $^{-1}$) that are generally necessary for ionic transport. This also eliminated the possibility in these initial scoping experiments of using lower frequency pulses, both cathodic and anodic, under square wave form (of which the power supply was capable) and comparing the results to known transient ionic conductivity behavior (16).

Most of the measurements, therefore, could be interpreted only in terms of electron flow.

b. Electronic Conductivity

Measurements of i_o , and of i_c where $i_o = V_{io}/10Q$ $i_c = V_{ic}/R_3$ (Figure 4) compile, from data of which Table IV is typical, to form the observations of Table V, from which the following can be inferred:

(1) Anodically grown films

The row responses in the anodized section of Table V support the previous inference from impedance measurements that the electrical analog of anodically grown ZrO_2 films

*The system polarity was established by noting on which pulse Cu^{++} was reduced on the working electrode, from which it was found that the upper half of the CRO traces corresponded to cathodic polarization of the working electrode.

LOW FREQUENCY FUNCTION GENERATOR
(HEWLETT PACKARD MODEL 202A)

FIG. 21-4. CONDUCTIVITY CIRCUIT

ZIRCALOY-2 FORMED TO 7.4 V (293⁰A).

$$R_2 = 1000 \Omega$$

$$V_c = .5 \text{ V/cm} \quad V_{ic} = .05 \text{ V/cm}$$

ZIRCALOY-2 FORMED TO 20 V (653⁰A)

$$R_2 = 1000 \Omega$$

$$V_c = .5 \text{ V/cm} \quad V_{ic} = .05 \text{ V/cm}$$

SAME CRO FORM FOR ALL OTHER SPECIMENS (EXCEPT 7.4 V) AT $R_2 = 1000 \Omega$

ZIRCALOY-2 FORMED TO 7.4 V

$$R_2 = 5500 \Omega$$

$$V_c = V_{ic} = 2 \text{ V/cm}$$

SAME CRO FORM FOR ALL OTHER SPECIMENS WITH $R_2 = 5500$ OR $R_2 = 10,000 \Omega$

FIG. 21-5. CRO TRACES DEPICTING ONSET OF CATHODIC CONDUCTION UNDER $\frac{1}{2}$ WAVE RECTIFICATION OF AC SIGNAL (ANODIC CYCLE REPRESSED). HORIZONTAL SWEEP = .4 sec/cm, CELL ELECTROLYTE: IN H_2SO_4

Typical Conduction Response (in $\text{I N H}_2\text{SO}_4$) To Signal and Circuitry of Figure 4, Schematically Shown at the Bottom of This Table. Values are Peak Currents, m A.

		Specimen														
		Anodized (Zirconium)						Steam Grown (1500 psi) (Zircaloy-2)								
		20 V (529 A°)		52 V (1377 A°)		130 V (3081 A°)		2 Days 440°C (12489 A°)		4 Days 440°C (17789 A°)		14 Days 400°C (22480 A°)		140 Days 400°C (100357 A°)		
		i _o	i _c	i _o	i _c	i _o	i _c	i _o	i _c	i _o	i _c	i _o	i _c	i _o	i _c	
i _c , cathodic/ anodic																
Cathodi- cally Pulsed	V _c															
	1.8	1.8	.002	1.8	.002	1.8	.006	1.9	.016	1.8	.01					
	7.6	2.2	.88	2.3	.88	2.2	.88	2.3	.8	1.9	.128					
AC Signal 5 Minutes After Cath- odically Pulsing	17.5	4.5	2.6	4.5	2.6	4.4	2.8	4.4	2.8	2.2	.3					
	1.8									.016/ .004						
	7.6							.52/ .04		-						
AC Signal Without Prior Cathodic Pulsing	17.5		1.84/ .08		1.6/ .12		1.6/ .12			.44/ .12						
	1.8					1.8	.006/ .006			1.8	.01/ .008	1.8	.002/ .006	1.7	0/0	
	7.6			2.2	.44/ .02	2.0	.3/ .002			1.9	.084/ .03	1.9	.064/ .014	1.8	.008/ .004	
	17.5			2.9	1.12/ .04	2.6	.8/ .002			2.0	.18/ .06	2.0	.088/ .014	1.8	.012/ .006

TABLE V

Behavior of Source Current, i_o , and Cell Current, i_c , as a
Function of Film Formation and Impressed Voltage, V_c ,
Across the Cell

		Signal			
		Cathodically Pulsed		AC	
		i_o	i_c	i_o	i_c
Anodized	Effect of Film Thickness at Given V_c $\partial/\partial L(i_o, i_c)$	0	0	-	-
	Effect of V_c at Given Film Thickness $\partial/\partial V_c(i_o, i_c)$	/	/	/	/
Steam Grown	Effect of Film Thickness at Given V_c	-	-	-	-
	Effect of V_c at Given Film Thickness	/ (thin) 0 (thick)	/	0	/

/ :: monotonic increase
- :: monotonic decrease
0 :: independence

can be represented by:

The fact that, under cathodic pulsing:

$$\partial/\partial L (i_o, i_c) = 0$$

$$\partial/\partial V_c (i_o, i_c) > 0$$

indicates that R_L , the resistance of the electronic leakage path, is independent of film thickness and that the values of R_2 and R_L are probably within 3 orders of magnitude of each other.

Under ac signal, the fact that:

$$\partial/\partial L (i_o, i_c) < 0$$

$$\partial/\partial V_c (i_o, i_c) > 0$$

is consistent with the RC impedance measurements, that is:

R_B and C_B are increasing with increasing film thickness.

(2) Steam grown films

The steam grown film responses in Table V support the presence of a crack network, and suggest the following analog:

where there are n RC components of unit geometric area projection of oxide film. Under cathodic pulsing the fact that:

$$\partial/\partial L (i_o, i_c) < 0$$

indicates that the leakage path resistance R_L is increasing with increasing film thickness and it is assumed to be due to the resistance of the electrolyte filled crack network. The increase of RC components resulting in:

$$\partial/\partial l (i_o, i_c) < 0$$

under ac signal is consistent with the previous impedance measurements. From an analog consistency viewpoint it is interesting to note that the capacity measurements of the steam grown films did not, through dissipation factor measurements, indicate a clear preference for:

as they did for the anodically grown films (at 1000 cps, the frequency at which the capacity measurements were made, the valve circuit $\dashv$ vanishes). Rather, they indicated that either

were acceptable to the measuring bridge.

The observation, under both cathodic pulsing and ac signals, that $\partial i_o / \partial V_c = 0$ is significant.

For, particularly under cathodic pulsing, it indicates that the cell leg impedance is so small compared to R_2 that regardless of how R_2 is varied the impedance of:

is unchanged. Since $R_3 = 5000$ and $R_2 \text{ max} = 10,000$ the cell leg impedance cannot be $\ll R_2$. Therefore, that

$\partial i_c / \partial V_c = 0$ in the case of the steam grown films is indicative of polarization control of the conduction phenomena under both cathodically pulsed and ac signals under particular circuitry of these experiments. This is not unreasonable in view of the crack net work in the steam grown films.

(3) Rectification considerations

Figure 6 indicates the presence of a substantial degree of anodic rectification, whose occurrence in oxide films has been generally summarized by Vermilyea (17) and by Young (18). Conduction behavior in the studies herein discussed tend to support the weak spot (19, 20) theory in the anodically grown films involving electronic leakage and semi-conductor (solid state) rectification rather than hydrogen reduction (electrolytic) rectification theories (21), for the following reasons:

- (a) Repeated cathodic pulsing did not result in film damage (at least as measured by RC impedance behavior) (22).
- (b) Zirconium developed a much better anodic "valve" oxide than did the zirconium-tin alloy, Table VI. It is conceivable that weak spots in the films are associated with impurity atom sites. The film growing over these could well have a composition somewhat different than that of the bulk, sound (by comparison

ZIRCALOY-2 FORMED TO 152 V (5156 A⁰) $V_c = .5$ V/cm $V_{ic} = .05$ V/cm.
2 sec/cm SWEEP. AC SIGNAL IMPRESSED AFTER 45 MINUTES OF CATHODIC
IMPRESSION, $R_2 = 1000 \Omega$ (ANODIC CYCLE REPRESSED BY $\frac{1}{2}$ WAVE
RECTIFICATION).

ZIRCALOY-2 FORMED TO 152 V (5156 A⁰), $V_c = .5$ V/cm $V_{ic} = .05$ V/cm.
1 sec/cm SWEEP. AC SIGNAL. NO PRIOR RECTIFICATION.
 $R_2 = 1000 \Omega$

ZIRCALOY-2 FORMED TO 152 V (5156 A⁰) $V_c = 5$ V/cm $V_{ic} = 2$ V/cm.
2 sec/cm SWEEP. AC SIGNAL IMPRESSED AFTER 120 MINUTES OF
CATHODIC IMPRESSION, $R_2 = 10,000 \Omega$ (ANODIC CYCLE REPRESSED BY
 $\frac{1}{2}$ WAVE RECTIFICATION)

ZIRCALOY-2 FORMED TO 152 V (5156 A⁰) $V_c = 5$ V/cm $V_{ic} = 2$ V/cm.
1 sec/cm SWEEP. AC SIGNAL. NO PRIOR RECTIFICATION $R_2 = 10,000 \Omega$

FIG. 21-6. EFFECT OF PRIOR RECTIFICATION (FORCED) ON SUBSEQUENT AC CONDUCTION BEHAVIOR OF ZrO_2
ANODICALLY GROWN ON ZIRCALOY-2. CELL ELECTROLYTE: IN H_2SO_4

TABLE VI

Anodic Rectification Efficiency, ϵ , of ZrO_2 Films Formed
Anodically and in Steam on Zircaloy 2 and on Zirconium.

ϵ = Vic cathodic / Vic anodic.

Material	Method of Film Formation	Voltage Division $R_2 \times 10^{-3}$		
		1	5.5	10
Zircaloy 2	Anodization in 1 N H_2SO_4 to			
	7.4 V (293 A°)	.4	-	-
	20 V (653 A°) (1)	1.5	-	3.3
	52 V (1745 A°) (1)	2.5	-	5.5
	152 V (5156 A°) (1)	1.2	-	7.6
	152 V (5156 A°) (2)	.5	10	15
	Exposed to 400°C (1500 psi) Steam - for			
	14 days (22480 A°)	.33	4.6	6.5
	140 days (100357 A°)	-	2	2
	Exposed to 440°C (1500 psi) Steam - for			
	2 days (12489 A°) (2)	-	13	-
	4 days (17789 A°) (2)	4	-	3.7
	4 days (17789 A°) (1)	1.3	2.8	3
Zirconium	Anodized in 1 N H_2SO_4 to			
	20 V (529 A°) (1)	-	-	23
	52 V (1377 A°) (1)	-	-	13.3
	52 V (1377 A°) (2)	-	22	28
	130 V (3081 A°) (1)	-	-	13.3
	130 V (3081 A°) (2)	1	150	400

(1) 5 minutes after 1/2 rectification of ac signal

(2) without prior rectification

to weak) film. As such the weak spot would constitute a type of "tendrill" projecting through the oxide film. The purer material would be expected to have fewer tendrills or conduction pipes of intrinsically low resistance and possibly low dielectric strengths.

(c) Rectification was sustained when mercury was the cell "electrolyte". In experiments involving mercury, rectification in relatively thin films rapidly broke down with the application of 17.5 volts across the cell leg (V_c), Figure 7. Thicker films sustained rectification in mercury for as long as they were so exposed (up to 72 hours) without apparent change in conduction behavior under 17.5 volts. However, when the thinner films were reimmersed in 1 N H_2SO_4 they immediately regained their valve characteristics. Several conclusions of interest may be inferred from these observations, and from rectification response to changing ac frequency:

i. The stability of the valve is field, rather than voltage, dependent.

ii. The nature of the valve could well be a p-n junction, with p-type semiconduction arising as a result of filling anion vacancies at the oxide-electrolyte interface, accompanied by the creation of electron defects by (23):

FIG. 21-7.

CONDUCTION BEHAVIOR OF ZIRCALOY -2 ANODIZED TO 20 V (653^0A) USING MERCURY AS THE "ELECTROLYTE". AC SIGNAL. SWEEP 2 SEC/CM.

Interfacial reactions may also promote a positive space charge due to the consumption of n-type oxide quasi free electrons in the chemisorption of oxygen. However, in view of the possibility of quasi free electron trapping by anion vacancies it is doubtful whether the space charge has any influence on conduction behavior (24). The absence of influence is indicated by the lack of proportionality between i_c and V_c^2 (Table IV).

Frequency effects tend to support the role of equation (1) in creating a p-n junction. Solid state devices in which p-n junctions are built in by doping to provide rectification will ordinarily continue to rectify at ac frequencies of around one megacycle per second or greater. In these experiments rectification essentially vanished at 100 cycles per second. This would arise with a depletion of adsorbed O_2 , as anodic polarization became less and less with increasing frequency, tending to throw the equilibrium of (1) to the left. The fact that rectification was never measurably complete indicates some anodic leakage due to incomplete filling of all anion vacancies in the oxide surface layers at the oxide-electrolyte interface.

That (1) was operative in the case of a specimen which after forming was stored in dry air before being immersed in mercury is not inconsistent. In this instance O_2 would be present due to VanderWaal's physical adsorption forces which would establish an equilibrium for (1) which mercury would not necessarily destroy.

Observations concerning ac behavior following cathodic pulsing also tend to support (1). Immediately upon switching to ac after cathodic pulsing the anodic and cathodic currents were nearly the same (Table IV lists the values after 5 minutes of an ac signal). As the ac signal continued, current flows in the anodic direction decreased until they reached some small values whose magnitudes compared to the cathodic currents were like those in Table VI. The explanation is, that during cathodic pulsing, oxygen polarization was destroyed, throwing (1) to the left. Vacancy filling upon ac signal impression required a finite time to bring (1) to equilibrium.

iii. The loss of rectification could result from a breakdown of the dielectric in the tendril region, reduction of the barrier in the anodic direction to permit electron injection into the space charge or field annihilation of the p-n junction. The experiments do not indicate which mechanism of rectification

breakdown is the most plausible, although the cathodic current perturbation in Figure 7a, b, suggests electron avalanching as a result of dielectric breakdown.

- (d) Comparison of cell voltage decay characteristics of a ZrO_2 working electrode to those of a smooth platinum working electrode indicated that hydrogen polarization of the working electrode was small in relationship to the double layer charge and the platinum auxiliary electrode anodic polarization (25).

Cell voltage decay characteristics were the same for anodically and steam formed films. In view of the preceding remarks about conduction behavior in the latter and of Vermilyea's recent dissertation (26) on the association of rectification with film flaws, and in the absence of any particular correlation between formation flaw and formation strain crack as discussed by Pemsler (27), it would appear as though the cracked model for steam grown films should be modified to read, schematically:

in which the number of R_2C_2 type-components is very much less than the number of R_1C_1 type-components.

IV. CONCLUSIONS

- A. Conduction measurements, under a specific experimental adaption of ac polarographic techniques, made on zirconium and on zirconium-tin alloy oxide films did not yield information regarding the nature of the hydrogen transport mechanism through the film as occurs during exposure to high temperature water.
- B. The measurements did suggest electronic leakage analogs, which tend to support tendril type leakage paths and associated rectification "valves", at least in the anodically grown films.

V. RECOMMENDATIONS

The experimental method is inexpensive and should be pursued under conditions which will test the hypothesis that free protons are present as charge carriers in zirconium alloy oxide films. Obvious improvements in experimental techniques include (1) a more refined cell geometry (28) equipped with reference electrodes so that potentials rather than ir drops may be measured, and (2) a modified variable frequency function generator that will provide for field strengths greater than 10^{+6} V cm⁻¹, under both triangular and square wave signal modes.

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HYDROGEN OVERVOLTAGE AT ZIRCONIUM INTERMETALLICS

by

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Hydrogen Overvoltage at Zirconium Intermetallics*

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ABSTRACT

Hydrogen overvoltage η , at zirconium and zirconium intermetallics has been measured in aqueous 1 M H_2SO_4 . Measurements have been made at 25°C over the current density range 10^{-5} - 1 amp cm^{-2} . The Tafel equations for these measurements as expressed in kinetic form are:

Zr	$i = 7.04 \times 10^{-7} \times \exp (2.303\eta/0.136)$
Zr ₂ Cu	$i = 1.86 \times 10^{-6} \times \exp (2.303\eta/0.153)$
Zr ₂ Ni	$i = 4.79 \times 10^{-7} \times \exp (2.303\eta/0.123)$
ZrV ₂	$i = 1.42 \times 10^{-6} \times \exp (2.303\eta/0.119)$
Zr-90 w/o Nb	$i = 5.44 \times 10^{-7} \times \exp (2.303\eta/0.096)$

A correlation of overvoltage with metal hydrogen bond strength is reported and a model for hydrogen pickup in unoxidized metals is discussed.

* This work was performed as part of the Joint U.S.-Euratom Research and Development Program under AEC Contract AT(04-3)-189, Project Agreement 24.

INTRODUCTION

The effects of various alloy additions on the hydrogen pickup phenomena in zirconium binary alloys have been studied by various workers.⁽¹⁻⁵⁾ In general, these studies have been empirical in nature and have not provided a general system of predicting the effects of alloy additions on the hydrogen pickup resulting from water or steam corrosion.

One of the major reasons for the lack of a consistent theory is the metallurgical structure of most zirconium alloys. Most commonly used alloying elements exhibit very limited solid solubility and high concentrations of intermetallic compounds. Consequently, it is necessary to determine whether hydrogen pickup is controlled by the limited solid solution, or by the intermetallic compounds. Berry, Vaugh and White⁽⁶⁾ have proposed that hydrogen pickup in zirconium alloys is controlled by the intermetallic compounds. On the other hand, Wanklyn⁽⁷⁾ has suggested that the alloying additions in solid solution control pickup and that the effects of increased alloying result from a more uniform compound distribution and consequently more homogeneous solid solution. In support of the former, are the facts that hydride needles and platelets have been observed in clusters around intermetallic particles, and that increasing intermetallic concentrations in the zirconium-iron, zirconium-copper and zirconium-nickel systems result in increased rates of hydrogen pickup.

In support of the second argument is the fact that increasing second phase concentrations resulting from additions of chromium, vanadium, antimony and tin show negligible increases in the rate of hydrogen pickup.

The purpose of the present experiments was to test the suggestions of Berry and his co-workers with respect to the electrochemical phenomenon known as hydrogen overvoltage. It is important to review the proposals of these authors before proceeding. As the result of a series of experiments, Berry and his co-workers suggested that hydrogen pickup resulting from the high temperature aqueous corrosion of zirconium alloys was related to the hydrogen overvoltage of the intermetallic particles present in the alloy matrix. They proposed that these particles were cathodic with respect to the matrix, thus promoting good corrosion resistance by anodic polarization. They further postulated that chromium iron and nickel intermetallics have low hydrogen

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overvoltage values and that hydrogen ions resulting from the corrosion reaction are discharged at these particles. In the case of the chromium and iron intermetallics the hydrogen atoms readily combine to form molecular hydrogen and are easily desorbed from the surface. However, in the case of the nickel intermetallic, the hydrogen atoms do not combine into molecular hydrogen, but remain on the particle surface and eventually migrate into the alloy under a thermally activated diffusion process. Many of these proposals are based on conjecture, and parallel the arguments of Greenblatt and Levy⁽⁸⁾ in the explanation of hydrogen pickup during the corrosion of aluminum alloys.

Consequently, it was necessary to measure the hydrogen overvoltage of the various zirconium intermetallic compounds in binary systems which show good, poor, and intermediate rates of hydrogen pickup. It was also necessary to measure whether or not the intermetallics are cathodic with respect to the alloy matrix.

Experimental Techniques

Specimen Preparation

Specimens suitable for overvoltage measurements were prepared from crystal bar zirconium and high purity alloying elements. Alloy preparation consisted of multiple melting in an inert atmosphere electric arc furnace. Alloys were prepared in 50 gram ingots and were melted a total of six separate times. Individual specimens were cut from the ingots with a high speed cutoff wheel and were shaped into rectangular prisms by grinding, polishing, and light chemical etching. One hole approximately 0.015 inch in diameter was drilled into each specimen. Platinum lead wires were then inserted into these holes and spot welded on the specimens.

Specimens prepared by this technique were Zr, Zr₂Ni, Zr₂Cu, ZrV₂, and Zr-90 w/o Nb. Efforts were made to prepare specimens of Zr Fe₂ and ZrCr₂; however, these alloys were extremely brittle and shattered repeatedly during fabrication.

Metallographic examination of the alloys revealed the structures shown in Figure 1. It is evident that all alloys exhibited uniformly dispersed second phases while the ZrV₂ alloy seems to contain three phases. Similar difficulty

in obtaining single phase alloys of zirconium intermetallics were encountered by Tobin and Pemsler in their studies.⁽⁹⁾

Overvoltage Apparatus

The overvoltage cell used in these experiments is shown in Figure 2. The cell was a one liter pyrex vessel which contained a thermometer well and four symmetrically placed standard-taper ground glass joints. A total of four electrodes were contained within this cell, the test electrode which consisted of one of the intermetallic specimens, a platinum anode, a saturated calomel standard electrode, and a Hildebrand-type hydrogen gas electrode.

Electrical power for the measurements was provided by two six volt batteries in series with a Simpson multirange ammeter and a combination of resistors and voltage dividers for current adjustment. A twelve volt battery charger was connected to the batteries prior to each measurement in order to assure a stable current supply.

Hydrogen gas was supplied to the Hildebrand electrode after passing through a drying and de-oxidizing train. Oxygen and other impurities were removed from the gas thus minimizing the possibility of "poisoning" the highly adsorbent platinized foil.

Overvoltage Measurement Techniques

Prior to each measurement, the entire cell was cleaned with an aqueous solution of 50% HNO_3 followed by hot 1 M H_2SO_4 and several washings with distilled water. The 1 M H_2SO_4 electrolyte was then purified by pre-electrolysis between platinum electrodes at 10^{-2} amp cm^{-2} for 24-48 hours. The intermetallic specimen was then inserted into the electrolyte and flashed for 30-60 seconds at a high current density in order to reduce surface oxides prior to measurement. During all measurements the electrolyte was continually agitated with a pyrex covered magnetic stirring rod, and with the bubbling action of hydrogen gas from the Hildebrand electrode.

Before measurements were started, the saturated calomel electrode was calibrated with respect to the hydrogen electrode. The Haber-Luggin capillary was then adjusted so that it was very close but not touching the specimen surface. A series of known currents were then passed between the specimen and

Zr₂ Ni - 250 X

Zr₂ Cu - 100 X

Zr V₂- 500 X

Zr - 90 w/o Nb - 150 X

Figure 1. ZIRCONIUM ALLOY STRUCTURES

Figure 2. HYDROGEN OVERVOLTAGE CELL

the platinum anode. The potential between the specimen and the calomel electrode was allowed to stabilize for 2-3 minutes at low current densities and 20 minutes at high current densities. Measurements of overvoltage were then made with a modified General Electric Recording Potentiometer, and calibrated with a Leeds and Northrup Volt Potentiometer. Two readings were taken at each current density measured, and temperature measurements were taken in order to apply corrections to the standard electrode potential. Current densities were calculated on the basis of apparent surface area and overvoltage values were obtained by subtracting the corrected calomel electrode potential from the measured emf.

Cell EMF Measurement Technique

Following the overvoltage measurements, the specimens were chemically etched and inserted into the electrolytic cell. The high purity 1 M H_2SO_4 solution was used as a electrolyte. The electromotive force produced by the cell was measured on a General Electric Recording Potentiometer, and calibrated on a Leeds and Northrup Volt Potentiometer. It was found the potentials produced by the cells $\text{Zr-Zr}_2\text{Cu}$ and $\text{Zr-Zr}_2\text{Ni}$ change with respect to time. Consequently, the measured potentials are reported as the initial stable potential.

RESULTS

Overvoltage Measurements

A plot of the hydrogen overvoltage (η) versus the logarithm of the current density ($\log i$) is shown in Figure 3. The kinetic forms of the Tafel equations for the alloys measured are listed below.

Zr	$i = 7.04 \times 10^{-7} \exp 2.303 \eta/0.136$
Zr_2Cu	$i = 1.86 \times 10^{-6} \exp 2.303 \eta/0.153$
Zr_2Ni	$i = 4.79 \times 10^{-7} \exp 2.303 \eta/0.123$
ZrV_2	$i = 1.42 \times 10^{-6} \exp 2.303 \eta/0.119$
Zr-90 w/c Nb	$i = 5.44 \times 10^{-7} \exp 2.303 \eta/0.096$

The general form of the above equation is:

$$i = i_0 \exp 2.303 \eta/b$$

where b is the slope of the linear portion of the curve, i_0 the current density at zero overvoltage, i and η the respective values of the current density and overvoltage.

Cell EMF Measurements

The potentials produced by the Zr-intermetallic cells in 1 M H_2SO_4 are shown in Table I.

TABLE I

<u>Material Polarity</u>		<u>EMF</u>
<u>+</u>	<u>-</u>	
Zr ₂ Cu	Zr	200-250 M.V.
Zr ₂ Ni	Zr	50-60 M.V.

DISCUSSION

Hydrogen Overvoltage and Hydrogen Pickup in Unoxidized Metals

Before discussing the measurements made during these experiments, it is first necessary to determine a relationship between hydrogen overvoltage and hydrogen pickup. A simple, frequently suggested mechanism for the hydrogen discharge reaction is the Volmer-Tafel mechanism.⁽¹⁰⁻¹²⁾ This reaction is divided into two basic steps, the "slow discharge" step I, and the catalytic desorption, step II.

The theoretical work of Bockis⁽¹²⁾ has shown that this mechanism is operative in strong acid solutions and current densities at which the Tafel slope is approximately 0.120. These conditions will hold for the present measurements.

The following argument will be used to demonstrate the correlation between high and low overvoltage measurements and the discreet steps in the Volmer-Tafel equation.

First, consider a material with a very low overvoltage, such as platinized platinum. This material in a hydrogen saturated solution has essentially zero overvoltage and is therefore used as the international standard for zero potential. The low overvoltage of this material is attributed to the ease

Figure 3. HYDROGEN OVERVOLTAGE VERSUS CURRENT DENSITY FOR ZIRCONIUM INTERMETALLICS

with which a small applied potential will produce an appreciable current. However, it is also well known that the heat of adsorption of atomic hydrogen on platinum is very high, finely ground platinum is widely used in many hydrogenation reactions in which molecular hydrogen must be dissociated.

Now, consider a material with a very high hydrogen overvoltage such as mercury or lead. A substantial potential must be applied before appreciable cathodic currents can flow at electrodes of these materials. This means that there is a large energy barrier opposing a proton transfer from the solution, across the Helmholtz double layer and subsequent discharge at the electrode surface. With respect to the catalytic desorption, it is well known that mercury and lead form very weak metal hydrogen bonds. Other materials will show intermediate behavior. This has been shown by Reütschi and Delahay.⁽¹³⁾ As seen in Figure 4, they have shown that there is an inverse linear relation between measured hydrogen overvoltage and the calculated heats of adsorption of atomic hydrogen. All overvoltage data shown in Figure 4 were measured by Bockris and his co-workers⁽¹⁴⁻¹¹⁾ and are generally considered to be the best available. The heats of adsorption were calculated on the basis of the Pauling equation,⁽¹⁸⁾

$$D(M-H) = \frac{1}{2} \{D(M-M) + D(H-H)\} + 23.06 (X_M - X_H)^2$$

in which $D(M-H)$, $D(M-M)$ and $D(H-H)$ are the respective bond energies of the metal-adsorbed hydrogen, metal-metal and hydrogen molecule. The X_M and X_H are the respective electronegativities of the metal and the hydrogen.

Reütschi and Delahay ignored the electronegativities in their calculations of the data shown in Figure 4. Their results which show that overvoltage decreases as $D(M-H)$ increases are qualitatively supported by Glasstone.⁽¹⁹⁾

Consequently, for the same steady-state discharge rate, i.e., the same current density, there will exist a higher surface concentration of adsorbed hydrogen at materials with strong (M-H) bonds than at materials with weak (M-H) bonds. Under the influence of thermal activation, diffusion of hydrogen will then occur at a high rate at the electrode with the strong (M-H) bond due to the higher surface concentration of adsorbed hydrogen. This analysis then leads to the conclusion that hydrogen pickup under identical discharge

Figure 4. HYDROGEN OVERVOLTAGE VERSUS HEAT OF ADSORPTION OF ATOMIC HYDROGEN FOR VARIOUS METALS. OVERVOLTAGE DATA FOR 1N HCL AT 25°C AND 10^{-3} amp-cm⁻². FROM REUTSCHI AND DELAHAY. (14)

conditions should be inversely related to the hydrogen overvoltage. Consequently, one can expect high rates of hydrogen pickup for the materials with low overvoltage and low rates of pickup for materials with high overvoltage.

This analysis requires that the energy barrier opposing the catalytic desorption and the energy barrier opposing the slow discharge must be governed by a more basic property of the material. This property is felt to be the electronic structure at the electrode surface.

On the basis of the above analysis and the present measurements, one would expect the highest rates of hydrogen pickup in Zr-90 w/o Nb and ZrV_2 , and the lowest in Zr, Zr_2Ni and Zr_2Cu . To say that these data are in disagreement with known corrosion pickup rates is premature. It is not definitely known whether the second phase particles in zirconium alloys control hydrogen pickup. If they do not, these measurements are generally inconclusive. Secondly, all present measurements were made on unoxidized specimens. It will first be necessary to measure the hydrogen overvoltage on solid solution alloys and their respective second phases in both the oxidized and unoxidized conditions.

Cell EMF Measurements

It is evident that the intermetallics studied are not cathodic with respect to the alloy matrix as proposed by Berry, et al.⁽⁶⁾ The potential produced by the zirconium - Zr_2Cu cell is approximately four times larger than that produced by the zirconium - Zr_2Ni cell. This indicates that during the early stages of corrosion, the zirconium-nickel alloys should corrode at a slower rate than the zirconium-copper alloys. This also indicates that the solid solution matrix will be the site of hydrogen discharge and adsorption during the first stages. It is interesting to note that Greenblatt and Atkinson⁽²⁰⁾ recently observed that the intermetallic compounds in aluminum alloys corrode at a faster rate than the matrix (i.e. the compounds are anodic) during the early stages of corrosion. This is in direct disagreement with the proposals of Greenblatt and Levy,⁽⁸⁾ who stated that intermetallic compounds are cathodic to the aluminum matrix and are the sites of major hydrogen pickup.

CONCLUSIONS

These measurements have shown that the relation between hydrogen pickup and hydrogen overvoltage is not as simple as that proposed by Berry, et al.⁽⁶⁾ During the early stages of zirconium alloy corrosion, the hydrogen discharge does not occur at the intermetallic particles, but rather at the alloy matrix. This statement only applies to the systems measured, zirconium-copper and zirconium-nickel. During later stages of corrosion, the hydrogen discharge may occur at the particles as the electrochemical polarities of the materials change.

A hydrogen discharge mechanism has been presented which is a function of the metal-hydrogen bond strength at the electrode surface. Although the η -(M-H) relationship (Fig. 4) applies only to pure, unoxidized metals, it may be seen that there is a qualitative agreement between this relationship and the effects of the pure metals additions on the hydrogen pickup rates resulting from zirconium alloy corrosion. This is based on the conclusion that low overvoltage materials have high pickup rates. Consequently, one would expect the highest pickup rates for binary zirconium alloys containing Pt, Pd, Au, Mo, Ta and N. And the lowest for those alloys containing Hg, Cd, and Pb. Other alloys would result in intermediate rates.

If one agrees with an inverse relationship between hydrogen overvoltage and hydrogen pickup one might conclude on the bases of Fig. 3, that hydrogen pickup should be highest in Zr-90 w/o Nb and lowest in crystal bar zirconium. However, measurements of hydrogen overvoltage on unoxidized second phase particles should not be extrapolated to explain hydrogen pickup through metal oxides at elevated temperatures.

One can only conclude that further work with an overvoltage technique would be of value. This work should include measurements of hydrogen overvoltage for oxidized and unoxidized solid solution alloys and their respective second phase particles. It should also include a study of the electrochemical potentials between the solid solution alloys and their respective second phases at various stages of corrosion.

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