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STUDIES OF THE HYDROGEN DAMAGE MECHANISM IN THE
CORROSION OF ZIRCONIUM

by

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
INTRODUCTION.	5
STUDIES OF THE CORROSION RATES AND HYDROGEN PICKUP OF ZIRCONIUM AND ZIRCONIUM ALLOYS IN AQUEOUS MEDIA . .	5
Experimental.	6
Zirconium in Water and CuSO_4 Solution	7
Zirconium Alloys in Water and CuSO_4 Solution.	7
CORROSION OF SINTERED COMPACTS OF ZIRCONIUM CON- TAINING CATHODIC INCLUSIONS.	13
General	13
Experimental.	13
Results.	14
CORROSION OF INTERMETALLIC COMPOUNDS WHICH COULD SERVE AS CATHODES	15
General	15
Experimental.	15
Results.	15
DISCUSSION	17
ACKNOWLEDGEMENT	19
REFERENCES.	20

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Corrosion Weight Gains in Water and in CuSO_4 Solution at 290°C . The solid lines are the data from water exposure. The shaded points are the data from CuSO_4 solution	7

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Corrosion Weight Gains of Zirconium in Water and in CuSO_4 Solution	6
II.	Corrosion Weight Losses of 0.5 w/o Ti Zirconium Alloys After 15 Hours at 350°C in Water and Various Solutions . . .	8
III.	Corrosion Data for Zirconium Alloys Containing 0.5 w/o Ti Plus Cathodic Additives - 15 Hours at 350°C	9
IV.	Hydrogen Contents of Control Specimens	10
V.	Hydrogen Contents of Zirconium Alloys after Corrosion . . .	11
VI.	Hydrogen Contents of Two Zirconium Alloys which were Abraded for Comparison with the Data of Table V	12
VII.	Results of Corrosion Testing Zirconium Compacts which were Sintered on Outgassed Molybdenum Sheet at 1200°C for 2 Hours	14
VIII.	Results of Corrosion Testing Zirconium Intermetallic "Compounds"	16
IX.	Appearance of Aluminum Intermetallic "Compounds" after Corrosion in Water.	16
X.	Corrosion Products Resulting from the Attack of Water on Various Zirconium Intermetallic Compounds.	17

STUDIES OF THE HYDROGEN DAMAGE MECHANISM IN THE CORROSION OF ZIRCONIUM

by

R. D. Misch

ABSTRACT

It is difficult to evaluate the effect of cathodic elements on the corrosion of zirconium in water because of the low corrosion rate. By the addition of 0.5 w/o of titanium, however, the oxidation of zirconium to ZrO_2 in 350°C water is increased, permitting a better relative evaluation of the effect of different cathodic elements.

Alloys containing 0.1 w/o iron, nickel, copper or platinum in addition to 0.5 w/o titanium have lower corrosion rates than the 0.5 w/o titanium alloy alone. The largest improvement derives from nickel and the least from platinum. The nickel alloy has the disadvantage of absorbing 90% of the corrosion hydrogen while the platinum alloy absorbs a negligible amount. The iron and copper alloys are intermediate in corrosion resistance and hydrogen absorption.

In the presence of oxidizing agents (CuSO_4 , CdSO_4 , I_2) the absorption of hydrogen diminishes and corrosion resistance shows a further improvement. These results are interpreted to indicate that hydrogen may be damaging within the oxide as well as at the metal-oxide interface.

Zirconium compacts, sintered with conducting dispersants, are inferior in corrosion resistance to arc-melted zirconium. The cathodes are beneficial only by comparison with zirconium controls sintered under the same conditions.

In complex alloys, cathodes may arise in a variety of ways and the corrosion resistance of the intermetallics may be of importance. Water can react with many compounds, e.g., ZrNi will form Ni and ZrO_2 . By contrast, the compound ZrFe_2 does not react rapidly. Iron may be of value because of the formation of this compound.

INTRODUCTION

Since the original suggestions by Draley and Ruther⁽¹⁾ and by Huddle,⁽²⁾ the importance of hydrogen in corrosion reactions with water has been emphasized by numerous investigators.^(3,4,5) The role of hydrogen in the corrosion reaction of zirconium is not defined satisfactorily because the impurities which are most deleterious, viz., N, Al, Ti, and C, have no obvious relation to the forming of cathodes on the surface. On the other hand, iron, nickel, and chromium are beneficial in small amounts, and iron and nickel have low hydrogen overvoltages, which means they can act as effective cathodes. Palladium is also a beneficial additive to zirconium.⁽⁶⁾ The cathodic theory is also supported by the fact that heat treatments producing a fine dispersion of the second phase are also favorable to corrosion resistance. It is possible that hydrogen is responsible for the increase in corrosion rate called transition, but there is no proof for this except the fact that hydrogen from the corrosion reaction is known to accumulate in zirconium and to precipitate as the hydride.

The effect of a conducting dispersant in aluminum was demonstrated by Ruther in the following way.⁽⁷⁾ Fused TiO_2 and ZrO_2 were crushed, sieved, and coextruded with pure aluminum to form materials with a dispersed second phase. The particles of TiO_2 were electrically conducting, whereas the ZrO_2 was insulating before and after exposure to water. The specimens containing TiO_2 particles were found to be more corrosion resistant than the specimens containing the ZrO_2 .

In view of these phenomena, several investigations of the hydrogen mechanism have been made by the Corrosion Group at Argonne. These studies used various zirconium alloys and corrosion media with the aim of influencing the hydrogen mechanism. Because of the small corrosion rate of zirconium, it is difficult to assess improvements in corrosion resistance. If the corrosion rate were increased, then differences could be measured in a relatively short time. This may be done by increasing temperature or adding a deleterious element, such as nitrogen, aluminum, or titanium. The addition of titanium was chosen in the present case because it is so chemically similar to zirconium and forms a complete series of solid solutions in the metal phase.

STUDIES OF THE CORROSION RATES AND HYDROGEN PICKUP OF ZIRCONIUM AND ZIRCONIUM ALLOYS IN AQUEOUS MEDIA

Experimental

Zirconium and titanium were used as iodide crystal bar. The iron, nickel, copper, and platinum were of electrolytic quality or better. After triply arc-melting in an inert atmosphere, the buttons, which weighed

approximately 10 grams each, were cold-rolled to a thickness of $\frac{1}{16}$ in. Discs with a diameter of $\frac{1}{2}$ in. were punched out, wet polished, and etched to a bright finish. Weighings were made on a microbalance.

To determine whether copper effectively displaces hydrogen under autoclave conditions, some aluminum powder was exposed to a copper sulfate solution for $4\frac{1}{2}$ hr at 290°C . This was sufficient to oxidize the aluminum completely. The weight of reduced copper indicated that the efficiency of reduction of copper was at least 80%, confirming the original expectation.

Zirconium in Water and CuSO_4 Solution

Zirconium was compared next in water and in CuSO_4 solution* at 350° for 15 hours. Each set of four specimens tarnished similarly, with interference colors being developed. The weight gains are shown in Table I.

Table I

CORROSION WEIGHT GAINS OF ZIRCONIUM IN WATER AND IN CuSO_4 SOLUTION

Medium	Specimen No.	Weight Gain, mg/dm^2
Water	1	5.1
	2	4.8
	3	5.0
	4	5.2
CuSO_4 Solution	5	5.1
	6	4.7
	7	11.6
	8	11.8

The two specimens having weight gains of 11.6 and 11.8 mg/dm^2 were not examined closely, but the weight increase may have resulted from debris from the autoclave. No copper crystals were observed. Judging by appearance, the copper sulfate had no effect.

An attempt was made to obtain the cathodic copper in an adherent form by spot-welding a short length of copper wire to each of two zirconium discs and exposing the specimens to CuSO_4 solution at 350°C for 15 hours.

*5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 80 ml of water slightly acidified with H_2SO_4 .

The experiment failed because the copper wires disappeared and left a residue of CuSO_4 crystals. Presumably, oxygen initially trapped in the autoclave was sufficient to oxidize the copper. The surface appearances of the zirconium specimens with and without the spot welds were the same except for the weldments. Both sets had interference colors. The presence of the copper wire evidently had no effect on the cathodic process.

Zirconium Alloys in Water and CuSO_4 Solution

Four zirconium alloys containing 0.05, 0.10, 0.25 and 0.50 w/o Ti were prepared by arc melting.

Corrosion data for three of these alloys in water at 290°C are shown in Figure 1. The corrosion rate obviously increased with concentration of titanium. In CuSO_4 solution, only one weight gain was measured for each specimen after 64 hours in CuSO_4 solution. Improvement was evident in the 0.10 w/o and 0.25 w/o alloys. Apparently, CuSO_4 had the largest influence when the corrosion rate was high.

Figure 1

Corrosion Weight Gains in Water and in CuSO_4 Solution at 290°C . The Dotted Lines Represent Weight Gains in Water. The Solid Lines are Data (Open Symbols) from CuSO_4 Solution.

Subsequent tests were carried out with the 0.5 w/o Ti alloy. This alloy corroded much faster than pure zirconium and formed a visibly thick oxide layer which was brittle. Consequently, it was possible to remove the oxide by bending the specimens until all the oxide flaked off. After bending, the metal surface was left with a very thin black film. This procedure was used with all the alloys containing 0.5 w/o titanium.

Specimens of 0.5 w/o Ti alloy were exposed to water and to solutions of CuSO_4 , CdSO_4 , and I_2 for 15 hours at 350°C . The results are shown in Table II.

All three solutions showed a diminution of corrosion rate as compared with that in pure water. After test, the control specimens were white, with multilayered flakes of oxide. The specimens out of the CuSO_4 solution were similar, but these had copper powder, leaf, or crystal nodules embedded in the oxide layers. Some of the copper crystals were 1 to 2 mm long. Similar deposits were not evident in the case of CdSO_4 .

Table II

CORROSION WEIGHT LOSSES OF 0.5 w/o Ti ZIRCONIUM
ALLOY AFTER 15 HOURS AT 350°C IN WATER AND
VARIOUS SOLUTIONS

Medium	Specimen No.	Metal Loss (mg/dm ²)	Average Loss	Comments
Water	1	2570	2650	White, flaking oxide
	2	2560		
	3	2700		
	4	2790		
	5	2960		
	6	2350		
	7	2650		
CuSO ₄ solution*	8	1510	1330	Copper particles were embedded in the white oxide
	9	1250		
	10	1220		
CdSO ₄ solution**	11	1612	1750	Yellowish, flaking oxide
	12	1880		
I ₂ solution†	13	1790	1880	White oxide
	14	1970		

*5 g CuSO₄·5H₂O in 80 ml water slightly acidified with H₂SO₄.

**5 g CdSO₄· $\frac{8}{3}$ H₂O in 80 ml water slightly acidified with H₂SO₄.

†5 g I₂ in 80 ml water.

Further comparisons were made with the 0.5 w/o Ti alloy to which 0.1 w/o of Fe, Ni, Cu, or Pt, respectively, were added. These alloys were compared in water and CuSO₄ solution, with the results shown in Table III.

In water, the corrosion resistance improved in the sequence: Pt, Cu, Fe, and Ni. In the CuSO₄ solution the sequence changed to Ni, Fe, Pt, and Cu. In the first case, nickel was the most effective additive with a corrosion weight loss of 1260 mg/dm² as compared with 2650 mg/dm² for the 0.5 w/o titanium alloy (Table II). In the second case, nickel was the least effective additive (1150 mg/dm²). No reason was evident for this change. In terms of atomic per cent, the iron, nickel, and copper were present in comparable amounts, and the platinum content was about one-third that of the others. Thus, platinum was the most effective additive on a mol basis.

Table III

CORROSION DATA FOR ZIRCONIUM ALLOYS CONTAINING 0.5 w/o Ti
PLUS CATHODIC ADDITIVES - 15 HOURS AT 350°C

Alloy	Medium	Metal Loss (mg/dm ²)	Average Loss	Comments
0.5 w/o Ti, 0.1 w/o Fe	Water	1500 1450	1480	Smooth, adherent, light grey oxide. Very slight edge flaking.
0.5 w/o Ti, 0.1 w/o Ni		1260 1260	1260	Smooth, adherent, light grey oxide. Very slight edge flaking.
0.5 w/o Ti, 0.1 w/o Cu		1790 1540	1670	Smooth, adherent, light grey oxide. Very slight edge flaking.
0.5 w/o Ti, 0.1 w/o Pt		2025	2025	Smooth, adherent, light grey oxide. Very slight edge flaking.
0.5 w/o Ti, 0.1 w/o Fe	CuSO ₄ * solution	1050 1010	1030	Finely divided white oxide; embedded Cu particles.
0.5 w/o Ti, 0.1 w/o Ni		1110 1190	1150	Finely divided white oxide; very few Cu particles.
0.5 w/o Ti, 0.1 w/o Cu		910 930	920	Finely divided white oxide; embedded Cu particles.
0.5 w/o Ti, 0.1 w/o Pt		970	970	Slight flaking; Cu particles visible under loose white flakes.

*5 g CuSO₄·5H₂O in 80 ml water slightly acidified with H₂SO₄.

After removing the oxide film, the above specimens were analyzed to determine the extent of hydrogen absorption. One specimen, representing each of the experimental conditions, was chosen for analysis. Pie-shaped segments were cut from each disc and were degreased and weighed. Each piece was placed in a graphite crucible supported by a sintered alumina crucible and was heated in an evacuated system. The temperature was brought to 1200°C, and the hydrogen was bled into a volume of 2.30 liters. The hydrogen pressure was measured with a calibrated thermocouple gauge and the gas was then pumped off. The procedure was repeated as often as necessary until the pressure had diminished to negligible proportions. The samples varied in weight from 0.1 to 0.4 gm.

The hydrogen levels of the blanks were evaluated by analyzing uncorroded specimens of arc-melted zirconium and Zr-0.5 w/o Ti alloy. After melting, the buttons were rolled but not etched or corrosion tested. The hydrogen content was found to vary from 36 to 172 ppm, as shown in Table IV. In addition, zirconium specimens which had been etched and corrosion tested were analyzed. The surfaces of these specimens had thin interference-color films. The hydrogen which may have been contributed by corrosion was not noticeable when comparing the results from the uncorroded and corroded specimens (see Table IV). The average hydrogen content for the uncorroded specimens was higher than the average for the corroded. Consequently, there is no evidence that any hydrogen was taken up, and the average for all eight specimens (80 ppm) was taken as the blank. It was concluded that outgassed zirconium would have been preferable for investigation, but the need for this was not realized until the corrosion results had been completed.

Table IV

HYDROGEN CONTENTS OF CONTROL SPECIMENS

Specimen	Medium	Hydrogen, ppm	Hydrogen Produced in Corro- sion, ppm
Zr	Uncorroded	69	-
		36	-
0.5 w/o Ti	Uncorroded	81	-
		172	-
Zr	Water, 15 hr at 350°C	80	17
		56	18
Zr	CuSO ₄ solu- tion, 15 hr at 350°C	64	17
		84	17

Table V shows the results for the 0.5 w/o Ti alloys after corrosion test. In this series, the minimum corrosion weight loss was 910 mg/dm² and the maximum was 2650 mg/dm². The hydrogen content, in terms of absorption from the corrosion reaction, could be estimated only when it exceeded 80 ppm. This occurred for the following alloys corroded in water: 0.5 w/o Ti alloy; 0.5 w/o Ti, 0.1 w/o Fe alloy; 0.5 w/o Ti, 0.1 w/o Ni alloy; and 0.5 w/o Ti, 0.1 w/o Cu alloy. The hydrogen contents of the remaining specimens (16 samples) averaged 43 ppm. The calculated absorptions after subtracting 80 ppm are listed in the last column of Table V. The dependence on medium and alloy composition was quite obvious. The 0.5 w/o Ti alloy absorbed 8% of the corrosion product hydrogen in water

but none when the media were oxidizing. The use of oxidizing solutions was evidently successful in changing the cathodic reaction from reduction of hydrogen to the reduction of CuSO_4 , CdSO_4 , or I_2 . The alloys showed a large increase in hydrogen pickup in water as compared with that of the 0.5 w/o Ti alloy, especially the alloy containing 0.1 w/o Ni. The platinum was exceptional because hydrogen pickup was negligible.

Table V

HYDROGEN CONTENTS OF ZIRCONIUM ALLOYS AFTER CORROSION

Alloy Composition	Medium	Specimen Weight Loss (mg/dm ²)	Hydrogen in Sample (ppm)	Hydrogen Produced in Corrosion (ppm)	Absorption (%)
0.5 w/o Ti	Water	2650	330 337	3300	7.6 7.8
0.5 w/o Ti	CuSO_4 solution	1220	37 34	1500	0
0.5 w/o Ti	CdSO_4 solution	1610	76 66	1900	0
0.5 w/o Ti	I_2 solution	1790	38 52	2400	0
0.5 w/o Ti, 0.1 w/o Fe	Water	1500	635 620	1700	33 32
0.5 w/o Ti, 0.1 w/o Ni	Water	1260	1310 1331	1460	84 86
0.5 w/o Ti, 0.1 w/o Cu	Water	1790	603 837	2100	25 36
0.5 w/o Ti, 0.1 w/o Pt	Water	2020	43 73	2400	0
0.5 w/o Ti, 0.1 w/o Fe	CuSO_4 solution	1010	17 28	1400	0
0.5 w/o Ti, 0.1 w/o Ni	CuSO_4 solution	1190	31 33	1740	0
0.5 w/o Ti, 0.1 w/o Cu	CuSO_4 solution	910	39 76	1200	0
0.5 w/o Ti, 0.1 w/o Pt	CuSO_4 solution	970	13 34	1140	0

When these alloys were tested in CuSO_4 solution, the hydrogen pickup dropped to negligible proportions in all cases. The hydrogen contents were often lower than 80 ppm, suggesting that hydrogen may have been lost at some point.

In all the above cases, the specimens were cut as segments and retained a very thin layer of unflaked oxide. A major portion of the hydrogen could have been trapped close to the surface, and the removal of this layer would have changed the results. This effect was verified for two specimens by wet polishing a segment lightly with 600 grit emery paper until all the oxide had been removed. The segments were then analyzed. The first sample was from the 0.5 w/o Ti alloy corroded in water, and the second was 0.5 w/o Ti, 0.1 w/o Fe corroded in water. A comparison with the original results is given in Table VI.

Table VI

HYDROGEN CONTENTS OF TWO ZIRCONIUM ALLOYS
WHICH WERE ABRADED FOR COMPARISON WITH
THE DATA OF TABLE V

Alloy Composition	Surface Treatment	Hydrogen in Sample (ppm)
0.5 w/o Ti corroded in water	Unabraded*	330 337
	Abraded	298
0.5 w/o Ti, 0.1 w/o Fe corroded in water	Unabraded*	635 620
	Abraded	436

*Data from Table V.

It is apparent that the concentration of hydrogen in the surface was much greater than that in the bulk; still, the major amount of gas existed in the bulk sample.

CORROSION OF SINTERED COMPACTS OF ZIRCONIUM CONTAINING CATHODIC INCLUSIONS

General

If a second phase is precipitated in an alloy, the solid solution can be expected to be saturated, and subsequent corrosion effects may result jointly from changes in composition of the matrix and the precipitate. The purpose of the present study was to separate these factors by introducing discrete cathodes by sintering instead of alloying.

Particles can be introduced into zirconium by sintering mixtures of zirconium hydride and another material. Provided the mixture does not react or interdiffuse, one can easily obtain discrete particles of a second phase dispersed in zirconium. To act as a cathode, the second phase should be an electronic conductor. In addition to metals, this requirement is met by carbides, nitrides, and many oxides. Only metals and oxides were used in this study because nitrogen and carbon are harmful to zirconium corrosion resistance. The choice of oxides to be used was based on differences in free energy of formation as compared with ZrO_2 to avoid reaction.

Experimental

The sintered compacts of zirconium plus additives were prepared from zirconium hydride* and various metal and oxide powders. The additives included: Mo, W, TiO_2 , Nb_2O_5 , SiO, Ta_2O_5 , ThO_2 and UO_2 . Zirconium hydride was used in preference to zirconium powder because it was safer to handle and had a lower oxide content. A ten-gram portion of zirconium hydride was mixed with 0.01, 0.1, 0.5 or 1.0 gm of the additive. The mixtures were pressed into $\frac{1}{2}$ -in. diameter pellets at 75 tons/in.² The pellets were sintered by induction heating in vacuum. According to Hausner and Kalish,⁽⁹⁾ complete densification (to 6.59 g/cm³) was obtained when ZrH_2 pellets, pressed at 75 tons/in.², were sintered for one hour at 1200°C. In this study all compacts were sintered for two hours at 1200°C. The temperature was measured by means of an optical pyrometer.

While bringing the compacts to temperature, the evolution of hydrogen raised the pressure temporarily in the vacuum system to 50 mm Hg. After the hydride had decomposed completely the vacuum improved rapidly and was 1×10^{-5} mm Hg at 1200°C. The specimens were supported on a sheet of molybdenum. The heater was a tantalum cylinder. The molybdenum sheet was outgassed by heating at 1450°C for one hour. Some of the oxides were probably a source of contamination because oxide powders usually

*Reactor grade, Metal Hydrides Co.

contain adsorbed air. The densities of three zirconium compacts measured after sintering at 1200°C for 2 hours were found to be 6.50, 6.44, and 6.49 gm/cm³. These values were comparable with that of arc-melted zirconium.

Results

After sintering, the metal compacts were wet-ground on 400 grit silicon carbide and corrosion tested in water at 350°C. One or more controls were always sintered under the same conditions. Typical results are shown in Table VII.

Table VII
RESULTS OF CORROSION TESTING ZIRCONIUM COMPACTS WHICH WERE
SINTERED ON OUTGASSED MOLYBDENUM SHEET**
AT 1200°C FOR 2 HOURS

Composition and Weight % of Additive Phase	Weight Gains and Appearance After Corrosion Testing in 350°C Water		
	76 hours		267 hours (All Specimens Losing Weight)
	Weight Gain, mg/dm ²	Appearance	Appearance
Pure Zr	24.6	Glossy black	Turning white; flaking on one edge
1.0% Mo (+400)*	19.6	Glossy black	Mottled light and dark grey oxide
4.9% Mo (+400)*	33.8	Slightly mottled; Mo particles clearly visible	Light grey, friable oxide layer
4.9% Nb ₂ O ₅ (+400)*	Wt. loss	White oxide intersper- spered with dark spots; cracks	Not tested
1.0% SiO (-325)*	60.0	Glossy black	Many tiny holes where the SiO was evidently leached out
1.0% Ta ₂ O ₅ (powder) (as-received)	23.8	Glossy black	Turning white; scattered bad spots
1.0% ThO ₂ (+400)*	41.3	Dull black basket- weave pattern in the oxide	White oxide in basket-weave pattern
1.0% UO ₂ (powder) (as-received)	78.3	Dull black basket- weave pattern in the oxide	Thin basket-weave white oxide plus many scattered white pustules
4.9% UO ₂ (powder) (as-received)	Wt. loss	Heavily mottled and basket-weave pattern; UO ₂ particles leached out	All white
4.9% fused UO ₂ (-80 +140)*	129.3	Heavily mottled and basket-weave pattern; UO ₂ particles leached out, plus dotted with yellow spots and cracks	Cracked and covered with oxide pustules

*The sign + (or -) indicates that the additive powder was retained (or passed) by a sieve of the indicated mesh.

**Outgassed at 1450°C for 2 hours.

Neither the controls nor the test specimens were comparable to good quality zirconium in corrosion resistance. With improved sintering it may be possible to demonstrate the value of inert cathodes. The present results do not show any advantage in terms of corrosion resistance.

CORROSION OF INTERMETALLIC COMPOUNDS WHICH COULD SERVE AS CATHODES

General

The second-phase constituents in high-zirconium binary alloys will consist of intermetallic compounds in nearly every case. If these compounds are to perform as effective cathodes, the compound should be stable in water, or the solid reaction product of the compound with water should be electrically conducting. Thus Schleicher⁽⁶⁾ showed that Zr_2Pd decomposed in water and palladium powder was formed. Coupling zirconium and palladium resulted in a decrease in corrosion rate.

Experimental

Several alloys corresponding to intermetallic compounds were prepared by arc-melting. The zirconium was iodide crystal bar, and the other metals were of commercial purity or better. The starting materials used in the arc-melting corresponded to the following compositions: ZrCo_2 , ZrCr_2 , Zr_2Cu , ZrFe_2 , ZrMo_2 , Zr_2Mn_3 , Zr_2Ni , ZrNi , ZrNi_3 , as well as 1 w/o Pt and 1 w/o Rh. All these alloys were melted twice with the exception of ZrCr_2 and ZrFe_2 , which shattered upon reheating. Consequently, these compositions were only used after one melting. Three compositions with aluminum were also prepared: ZrAl_3 , TiAl_3 , and NiAl . These were considered as possible additives to sintered compacts of zirconium.

None of these preparations was expected to have an ideal composition after melting, but enough compound formation was anticipated to permit a relative comparison of corrosion resistance. After etching, the arc-melted buttons varied in appearance from Zr_2Cu and ZrFe_2 , which had a uniform appearance, to ZrNi_3 which was badly segregated.

Results

All these "compounds" plus the platinum and rhodium alloys were tested in water at 290°C and 350°C. Evaluation was made solely on the basis of surface appearance. The "compounds" were exposed first to water at 290°C and, if they proved to be resistant, they were then transferred to water at 350°C. Because weight gains were not measured, the specimens were not cleaned before transferring to 350°C. The results are presented in Table VIII.

Table VIII

RESULTS OF CORROSION TESTING ZIRCONIUM INTERMETALLIC
"COMPOUNDS" IN WATER

Nominal Composition	290°C		350°C			Nature of the Corrosion Product
	2 hr	9 $\frac{1}{2}$ hr	3 hr	19 hr	83 hr	
ZrCo ₂	Interference Colors	Dull black film	Disintegrated	-	-	Ferromagnetic
ZrCr ₂		Dark grey	Dark grey	White	Grey, friable layer*	-
Zr ₂ Cu		Dark grey	Spalling	Coppery appearance, spalling	Disintegrated	Coppery brown
ZrFe ₂		Fragmenting	Disintegrated	-	-	Black chunks and powder ferromagnetic
ZrMo ₂		Dull brown film	Dark grey, spalling	Spalling	Fragmented (completely oxidized)	-
Zr ₂ Mn ₃		Grey	Grey	Powdery brown film	Powdery brown film*	
Zr ₂ Ni		Black	Disintegrated	-	-	Black powder ferromagnetic
ZrNi		Black	Dull black	Dull black	Disintegrated	Black powder ferromagnetic
1 w/o Pt		Interference colors	Interference colors	Shiny dark film, interference colors	Dark, iridescent film	-
1 w/o Rh		Interference colors	Interference colors	Shiny dark film, interference colors	Dark, iridescent film	-

*The bulk of the specimens were intact.

The aluminum intermetallics were exposed for slightly different times and the results are given in Table IX.

Table IX

APPEARANCE OF ALUMINUM INTERMETALLIC "COMPOUNDS"
AFTER CORROSION IN WATER

Compound	Time, hours				
	At 290°C		At 350°C		
	4	19	6	22	117
ZrAl ₃	No Apparent film	Disintegrated except for a small core	Further breakup	Powder	-
TiAl ₃	Golden-brown	Dark film good appearance	Dark film	Dark film	Dull black
NiAl	Bluish	Dark film good appearance	Dark film	Dark film	Negligible change

The corrosion products from all the intermetallic compounds were analyzed by the X-ray powder method, with the exception of Zr_2Mn_3 and ZrCr_2 , which had not disintegrated. The results are shown in Table X. The intermetallic compound survived water exposure in one case, namely, ZrFe_2 . The fact that a powder had formed was attributed to a nonhomogeneous structure in the original preparation. The arc-melted button was found to have a pearlitic structure in which the water attacked between the lamellae, removing the support for the intermetallic particles.

Table X

CORROSION PRODUCTS RESULTING FROM THE ATTACK OF
WATER ON VARIOUS ZIRCONIUM INTERMETALLIC
"COMPOUNDS"

Inter-metallic Compound	Products Observed in the Residue
ZrCr_2	Not determined
ZrCo_2	ZrO_2 ; some weak extra lines
Zr_2Cu	ZrO_2 ; weak lines for Cu; no Cu_2O or CuO
ZrFe_2	ZrFe_2 ; no ZrO_2 , Fe, FeO , or Fe_3O_4
Zr_2Mn_3	Not determined
ZrMo_2	Only ZrO_2
Zr_2Ni	Lines for ZrO_2 and Ni; no NiO
ZrNi	Lines for ZrO_2 and Ni; no NiO

DISCUSSION

The value of cathodes in the corrosion of zirconium has been demonstrated, but the exact nature of this protection is not clear. The data indicate that hydrogen liberation is deleterious in some way to the corrosion resistance of zirconium. The effect may be mechanical failure of the film, as suggested by Draley and Ruther,⁽¹⁾ or may involve other factors indirectly linked to hydrogen.

In terms of eliminating hydrogen and promoting corrosion resistance there are two mechanisms which may be important. The first is a catalytic mechanism in which the rapid combination of H to H_2 at the cathode surface prevents hydrogen diffusion into the film and metal. The second is a getter mechanism in which atomic hydrogen is absorbed by a second phase and consequently cannot cause damage. The getter theory was proposed by Draley⁽¹⁰⁾ to explain some aspects of uranium alloy corrosion. The importance of hydride precipitation in producing discontinuous failure in gamma-phase uranium alloys was discussed thoroughly by Burkart.⁽¹¹⁾ He pointed out that a Zircaloy clad would act as a hydrogen getter and prolong the life of defected fuel elements.

The catalytic mechanism is probably valid for the platinum alloy because the hydrogen absorption was negligible. This is understandable because platinum is well known as a catalyst for the reaction:

The other alloys containing iron, nickel, and copper absorbed more hydrogen than the control. Therefore, these metals cannot be effective by the catalytic mechanism alone. The getter mechanism seems reasonable because the nickel alloy, which absorbed the most hydrogen, had the lowest corrosion rate. The zirconium-nickel compound ZrNi has been shown to have a high capacity for hydrogen absorption.⁽¹²⁾ This may account for the difference between nickel and the other metals.

The catalytic theory assumes that the cathodes liberate hydrogen outside the oxide film. However, a dispersed cathodic phase will probably lose electrical contact with the metal when it is incorporated into the growing oxide. Molecular hydrogen will be formed beneath the oxide although not penetrating the metal. This mechanism is suggested as the reason why platinum was less effective than iron, nickel, or copper in decreasing corrosion, although it was very effective in keeping out hydrogen. If the iron, nickel, and copper intermetallic compounds were getters in both the metal and oxide, they would be better able to keep hydrogen out of the oxide.

When oxidizing agents were added to the water, the absorbed hydrogen dropped to negligible proportions in all cases. The corrosion rate diminished also, but to a much smaller extent. Although platinum in the alloy and oxidizing agents in the water were both effective in eliminating the absorption of hydrogen, the oxidizing agents improved the corrosion resistance more than the platinum.

Whereas the nickel alloy had the best corrosion resistance in water, it improved only slightly in copper sulfate solution and was surpassed by the iron, copper, and platinum alloys. No reason for this can be suggested on the basis of the hydrogen analyses, because hydrogen pickup was negligible for all four alloys in copper sulfate solution. These results indicate that each alloying element probably causes several simultaneous changes in the corrosion mechanism.

The effect of $CuSO_4$ on the platinum alloy was particularly interesting because the corrosion rate diminished to less than half its value in water. The hydrogen pickup of the platinum alloy remained low in both water and $CuSO_4$ solution. This result is evidence that the penetration of hydrogen to the metal-oxide interface is not the entire story, and the presence of hydrogen into the oxide layer may play an important part in

the corrosion mechanism. Hydrogen could penetrate into the oxide without reaching the metal-oxide interface. The iron, nickel, and copper alloys may drive their effectiveness from a combination of cathodic effectiveness and hydrogen gettering.

Effective corrosion protection may depend more on keeping hydrogen out of the oxide than out of the alloy. The proper alloying additives may render the oxide less susceptible to degradation by hydrogen. A deleterious additive, such as titanium, may produce a certain type of defect with which hydrogen can associate. By absorbing hydrogen, a ZrO_2 film with such defects might change in such a way as to promote diffusion or change the film structurally. As shown by Leach,⁽³⁾ the conductivity of UO_2 films is influenced by the presence of hydrogen.

The alloying elements of Zircaloy-2 may serve to control the defect structure of the ZrO_2 layer to minimize the accumulation of hydrogen. In high-temperature steam, in which the purity of zirconium no longer assures good corrosion resistance, alloying elements may be necessary to suppress or modify the formation of intrinsic defects.

This theory does not attempt to explain all aspects of zirconium corrosion but only the accelerating action of water or steam compared to dry oxygen. Unfortunately, the interpretation of zirconium scaling in dry oxygen has not reached the point where it can serve as a basis for interpreting data in water or steam.

Of the various methods of producing cathodes, alloying was the easiest and least objectionable. Sintering offered no advantage because good corrosion resistance was not obtained. Alloys containing intermetallic compounds should also be judged on the basis of the corrosion resistance of the compounds. If such compounds decompose in water, then protection presumably comes from the residue of metal powder or from compositional modification of the corrosion product.

The use of copper sulfate solutions indicated that some advantage was obtainable if oxidizing agents were present in the water. The usefulness of such agents was not a result of electrodeposited cathodes as may be observed from the fact that iodine had the same effect as copper whereas cadmium, which has a high overvoltage, would not be expected to be an effective cathode. These data suggest that the addition of oxygen might be helpful in diminishing hydrogen absorption during corrosion.

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