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THE EFFECT OF ALLOYING ADDITIONS ON THE PROPERTIES OF ZIRCONIUM AND ITS ALLOYS

by

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PHYSICAL METALLURGY DIVISION

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SUMMARY

The effect of additions of 0.1% Ce, 0.1% Y, 0.1% Au and 0.01-1.0% Ga on the tensile strength and corrosion behaviour of zirconium, Zircaloy-2 and Zircaloy-4 was investigated.

Additions of cerium and yttrium effected some increase in the tensile strength of zirconium and Zircaloy-4, and additions of gallium improved the tensile strength of zirconium.

Hydrogen absorption during corrosion by the Zr-0.1% Ce-0.1% Y alloy was reduced by addition of 0.1% Au, and the corrosion resistance of zirconium was improved by gallium additions.

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1. INTRODUCTION

This work is part of a general programme aimed at the development of improved zirconium alloys for nuclear applications.

Little information has been reported on the effect of the rare earth elements cerium and yttrium on the properties of zirconium and its alloys, and the present work was undertaken to explore the influence of minor amounts of these elements.

The effect of gold additions was investigated as part of a programme directed to the development of applications for this metal. Improvement in corrosion resistance similar to that obtained by the addition of noble metals to titanium was considered possible[1].

Gallium forms a highly self-protective oxide film and it was thought that this useful property might be imparted to alloys in which it was present, with consequent improvement in their corrosion resistance.

2. PREPARATION OF TEST MATERIAL

2.1 Preparation of Alloys

Table 1 lists the purity and source of the metals used in preparing the alloys.

TABLE 1

Alloying Materials

Material	Purity	Source
Crystal bar zirconium	99.9+%	Foote Mineral Co.
Sponge zirconium	Reactor Grade	Carborundum Metals Co.
Zircaloy-2	Reactor Grade	Tubing (ex Atomic Energy of Canada Ltd.)
Nickel	99.9%	International Nickel Co. of Canada Ltd.
Iron	99.9% (electrolytic)	A.D. McKay Ltd.
Chromium	99.0%	Shieldalloy Corporation
Yttrium	99.9%	American Potash and Chemical Corporation
Cerium	99.9%	American Potash and Chemical Corporation
Gold	99.9+%	Handy and Harman of Canada Ltd.
Gallium	99.999%	Alcoa International Inc.

The alloys were prepared in a tungsten-arc furnace in which the metal charge was melted by striking an arc between a tungsten electrode and the charge contained in a water-cooled copper hearth. Melting was carried out in an argon atmosphere at a pressure of 350 mm mercury and each lot was re-melted three times to ensure homogeneity. The resulting ingot was "cigar-shaped" and weighed about 75 g. Table 2 lists the compositions of the alloys prepared.

TABLE 2

Nominal Composition of Alloys Investigated

Ident.	Nominal Composition (wt %)*				Base Material
	Ce	Y	Au	Ga	
DO	0.1	-	-	-	Crystal Bar Zr
DW	0.1	-	-	-	Zircaloy-2
EB	0.1	-	-	-	Zircaloy-4
DP	-	0.1	-	-	Crystal Bar Zr
DX	-	0.1	-	-	Zircaloy-2
EC	-	0.1	-	-	Zircaloy-4
DQ	0.1	0.1	-	-	Crystal Bar Zr
DY	0.1	0.1	-	-	Zircaloy-2
ED	0.1	0.1	-	-	Zircaloy-4
DR	0.1	0.1	0.1	-	Crystal Bar Zr
DZ	0.1	0.1	0.1	-	Zircaloy-2
EE	0.1	0.1	0.1	-	Zircaloy-4
GL	-	-	-	0.01	Sponge Zr
GO	-	-	-	0.01	Zircaloy-2
GM	-	-	-	0.10	Sponge Zr
GP	-	-	-	0.10	Zircaloy-2
GN	-	-	-	1.0	Sponge Zr
GQ	-	-	-	1.0	Zircaloy-2
DN	Crystal Bar Zr				----------
FZ	Sponge Zr				----------
DV	Zircaloy-2				Sponge Zr
GR	Zircaloy-2				----------
EA	Zircaloy-4				Sponge Zr

*The alloys prepared using Zircaloy-2 or Zircaloy-4 as base material also contained the alloying elements present in those two alloys (see page 4).

As shown in Table 2, four different "base materials" were used in preparing the alloys, viz. crystal bar zirconium, sponge zirconium, Zircaloy-2 and Zircaloy-4. The two latter materials are zirconium-base alloys with the following nominal compositions:

	Weight, Per Cent					
	Sn	Fe	Cr	Ni	O	Zr
Zircaloy-2	1.20- 1.70	0.07- 0.20	0.05- 0.15	0.03- 0.08	0.10- 0.140	Balance
Zircaloy-4	1.20- 1.70	0.12- 0.18	0.05- 0.15	0.004- Max.	0.10- 0.140	Balance

The Zircaloy-2 and Zircaloy-4 alloys containing additions of cerium, yttrium and gold were prepared in the laboratory using sponge zirconium, whereas the Zircaloy-2 used as base material for the gallium alloys was taken from a length of commercially produced tubing.

Weights of the arc-melted alloys before and after alloying were so close as to justify the assumption that the required compositions had been obtained. For example, melt DR had a total weight of 72.4500 g before arc melting and lost 0.0021 g on melting for a weight change of 0.003%. As further assurance that the nominal compositions were correct, the gold in melts DR, DZ and EE assayed 0.1%*.

2.2 Fabrication of Alloys

All ingots were swaged to 0.35 in. diameter rod and part of each rod was rolled to 0.2 in. sheet. With the exception of the ingots prepared from crystal bar zirconium (DO, DP, DQ, DR and DN, which could be fabricated at room temperature), all other ingots were swaged and rolled at 500°C (930°F). To provide mechanical test specimens, a piece was cut from each swaged rod and annealed at 750°C (1380°F) for 1/2 hr in Houghton 980 salt, followed by water quenching. The rolled strip was similarly annealed after fabrication.

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*Assay carried out by Analytical Chemistry Subdivision of Mineral Sciences Division, Report No. MS-AC-63-949.

The Zircaloy-2 + 1.0% Ga alloy broke up on rolling, and consequently no test results can be reported for this material. The Zr-1.0% Ga composition cracked on rolling, but it was still possible to obtain corrosion specimens from the sheet.

2.3 Test Specimens

Hounsfield tensile specimens with 0.447 in. gauge length and 0.126 in. gauge diameter were machined from the annealed swaged rods.

Specimens for corrosion testing were prepared as 1 in.x5/16 in.x5/64 in. coupons from the annealed strip material.

3. EXPERIMENTAL PROCEDURE AND RESULTS

The alloys were tested by determining the tensile properties at room temperature, and the corrosion behaviour (including hydrogen absorption) in steam.

3.1 Tensile Tests

Room temperature tensile tests were carried out and results are listed in Table 3. All results are the average of two tests except in the case of melt GQ (Zircaloy-2 + 1.0% Ga) for which only one test specimen was available.

3.2 Corrosion Tests

Corrosion tests were conducted in an autoclave on duplicate specimens which were exposed to steam at 400°C (750°F) at 1500 psi. The de-ionized water used in the tests was changed each time the specimens were removed for weighing during the course of the test. All samples were tested in the same autoclave but in four separate batches, namely:

(a) crystalbar zirconium unalloyed, and alloyed with cerium, yttrium and gold.

(b) Zircaloy-2, and Zircaloy-2 alloyed with cerium, yttrium and gold.

(c) Zircaloy-4, and Zircaloy-4 alloyed with cerium, yttrium and gold.

(d) unalloyed sponge zirconium and Zircaloy-2; sponge zirconium and Zircaloy-2 alloyed with gallium.

The increase in hydrogen content of the test specimens during corrosion was determined by carrying out duplicate gas analyses on samples before and after corrosion testing.

TABLE 3

Tensile Properties of Zirconium and Zirconium Alloys

Melt Ident.	Composition	UTS kpsi	0.2% YS kpsi	% El. 4 $\sqrt{Area}$
DN	Crystal Bar Zr (CB)	30.1	18.1	28
DO	CB + 0.1% Ce	46.0	30.1	25
DP	CB + 0.1% Y	48.0	32.7	26
DQ	CB + 0.1% Ce + 0.1% Y	43.0	35.4	20
DW	Zr-2 + 0.1% Ce	78.6	57.7	19
DX	Zr-2 + 0.1% Y	76.0	61.8	21
DY	Zr-2 + 0.1% Ce + 0.1% Y	73.4	49.5	18
DZ	Zr-2 + 0.1% Ce + 0.1% Y + 0.1% Au	65.5	46.0	18
EA	Zircaloy-4 (Zr-4)	71.8	50.2	30
EB	Zr-4 + 0.1% Ce	71.1	57.5	27
EC	Zr-4 + 0.1% Y	75.2	57.0	29
ED	Zr-4 + 0.1% Ce + 0.1% Y	81.3	64.8	29
EE	Zr-4 + 0.1% Ce + 0.1% Y + 0.1% Au	73.8	56.2	29
FZ	Sponge Zr (Zr)	64.8	36.0	28
GL	Zr + 0.01% Ga	69.2	43.1	27
GM	Zr + 0.1% Ga	72.2	46.1	28
GN	Zr + 1.0% Ga	80.5	54.0	25
GR	Zircaloy-2 (Zr-2)	77.1	50.5	26
GO	Zr-2 + 0.01% Ga	75.5	51.4	26
GP	Zr-2 + 0.1% Ga	80.1	53.4	27
GQ	Zr-2 + 1.0% Ga	89.6	60.9	22

After exposure to steam for 144 hr the alloys of crystal bar zirconium with cerium, yttrium, and gold were covered with a heavy white corrosion film that spalled and broke off, making it impossible to determine accurately the weight gain and hydrogen pick-up, and consequently no corrosion results are given for these alloys. The specimens of sponge zirconium also began to lose weight after corrosion testing for 152 hr and no results are given for this material either.

The corrosion results are given in Figures 1, 2, and 3 as plots of weight gain of sample (in mg/dm^2) against hours of exposure to steam.

Figure 1 shows the effect of additions of 0.1% Ce, 0.1% Y and 0.1% Au on the corrosion of Zircaloy-4. Because of the similarity between the results, only two of the curves are drawn, namely those for Zircaloy-4 and Zircaloy-4 + 0.1% Ce + 0.1% Y.

Figure 2 gives the results for Zircaloy-2 and Zircaloy-2 containing 0.1% Ce, 0.1% Y and 0.1% Au. Again, as the results are close together, only the curves for Zircaloy-2 and Zircaloy-2 + 0.1% Ce + 0.1% Y are drawn.

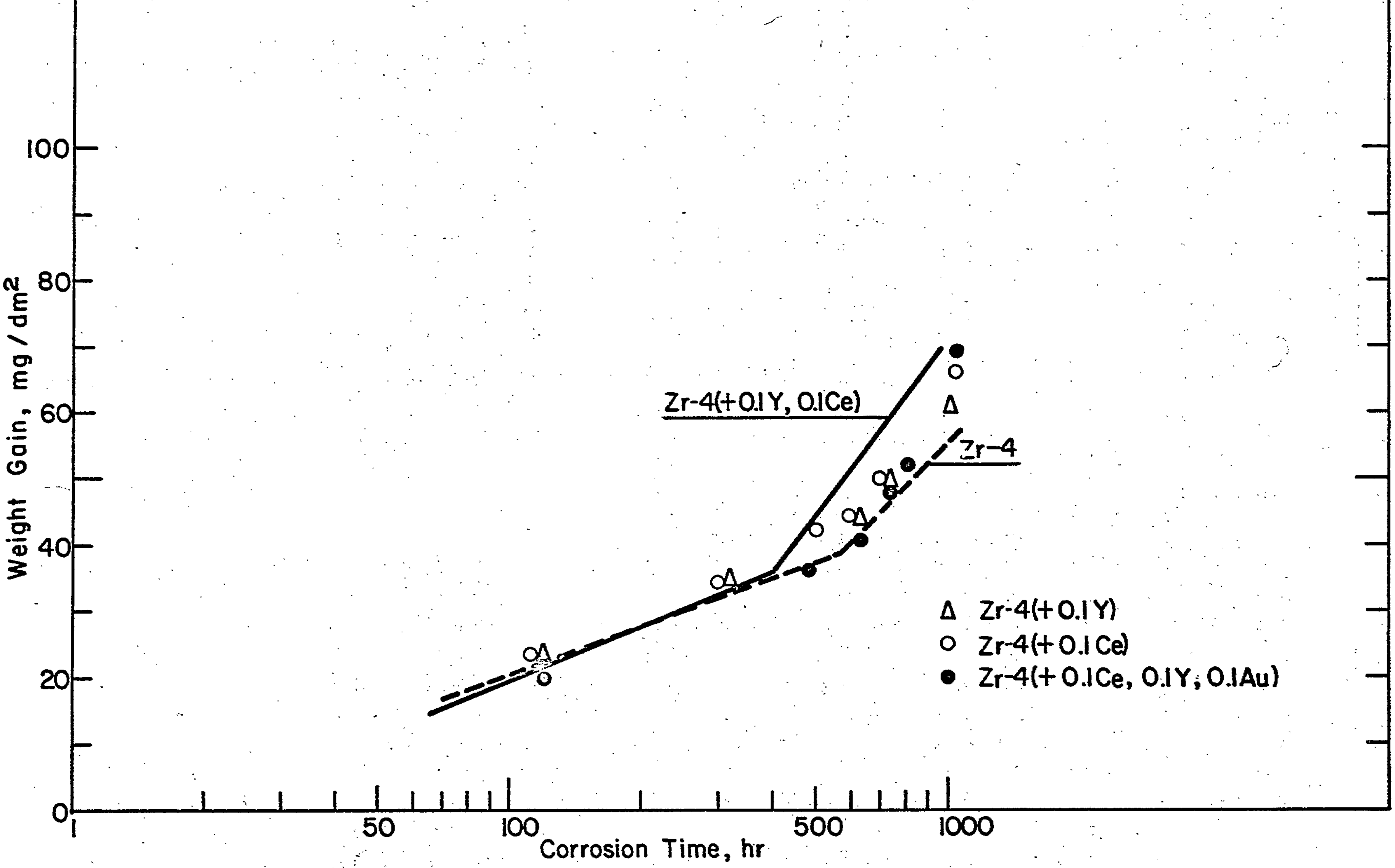
The corrosion results for Zircaloy-2 with and without gallium, and for zirconium with gallium are plotted in Figure 3.

Table 4 lists the time to transition and weight gain at transition, both taken from Figures 1, 2, and 3.

3.3 Hydrogen Absorption

Samples, before and after corrosion testing, were analysed for hydrogen to determine how much had been absorbed by the alloys during corrosion. The sub-fusion vacuum method was carried out on duplicate samples and the results are listed in Table 5. Besides the hydrogen content, Table 5 also gives the percentage of total available hydrogen actually absorbed by the alloys during corrosion. However the total available hydrogen could not be calculated for the samples that spalled during testing because it was not possible to determine their weight gain. These samples are marked with an asterisk in Table 5.

Figure I Corrosion of Zr-4 Containing 0.1wt% Ce, Y and Au
at 400°C (750°F) and 1500psi



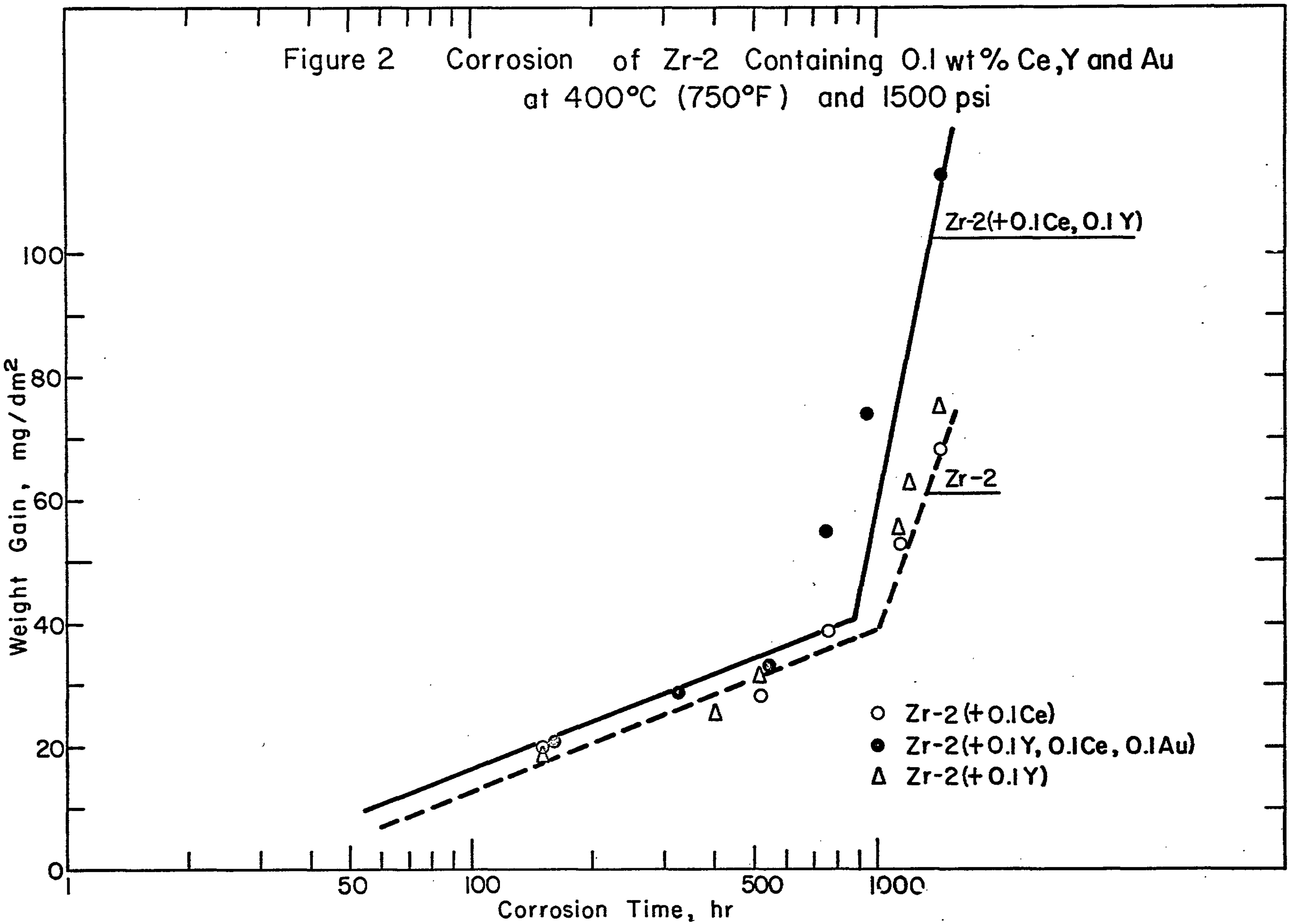


Figure 2 Corrosion of Zr-2 Containing 0.1 wt% Ce, Y and Au at 400°C (750°F) and 1500 psi

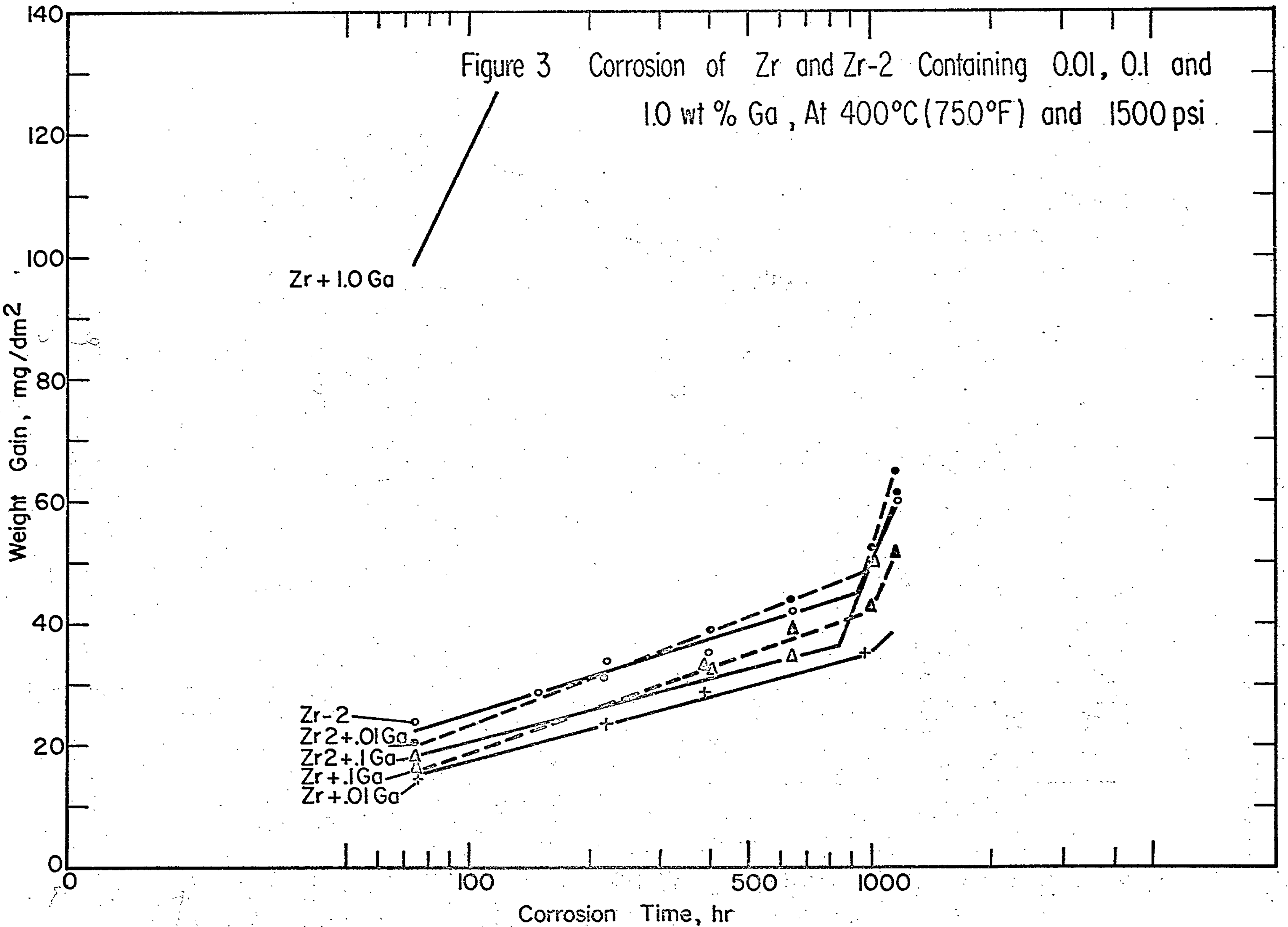


Figure 3 Corrosion of Zr and Zr-2 Containing 0.01, 0.1 and 1.0 wt % Ga, At 400°C (750°F) and 1500 psi

TABLE 4

Results of Corrosion Tests

(Steam at 400°C (750°F) and 1500 psi)

Alloy	Time to Transition (hours)	Weight Gain at Transition (mg/dm^2)
Zr-2	1000	39
Zr-2 + 0.1% Ce	840	31
Zr-2 + 0.1% Y	860	34
Zr-2 + 0.1% Ce + 0.1% Y	900	41
Zr-2 + 0.1% Ce + 0.1% Y + 0.1% Au	600	34
Zr-4	580	39
Zr-4 + 0.1% Ce	540	41
Zr-4 + 0.1% Y	580	42
Zr-4 + 0.1% Ce + 0.1% Y	410	36
Zr-4 + 0.1% Ce + 0.1% Y + 0.1% Au	640	39
Zr-2	920	45
Zr-2 + 0.01% Ga	960	48
Zr-2 + 0.10% Ga	840	36
Zr	<152	-
Zr + 0.01% Ga	980	35
Zr + 0.10% Ga	1000	42
Zr + 1.0% Ga	< 72	-

TABLE 5

Hydrogen Absorption by Zirconium and Zirconium Alloys
During Corrosion in Steam at 400°C (750°F) and 1500 psi

Melt Ident.	Alloy	Hydrogen Content (wt %)		Hydrogen Absorption (as % of Total Available)	Duration of Test (hr)
		Before Corrosion	After Corrosion		
DN	Crystal Bar Zirconium (C.B.)	0.0056	0.0580	-	144*
DO	C.B. + 0.1 Ce	0.0064	0.0800	-	144*
DP	C.B. + 0.1 Y	0.0055	0.1240	-	144*
DQ	C.B. + 0.1 Ce + 0.1 Y	0.0076	0.1300	-	144*
DR	C.B. 0.1 Ce + 0.1 Y + 0.1 Au	0.0039	0.0700	-	144*
DV	Zr-2	0.0036	0.0077	22	1466
DW	Zr-2 + 0.1 Ce	0.0041	0.0100	29	1466
DX	Zr-2 + 0.1 Y	0.0035	0.0100	31	1466
DY	Zr-2 + 0.1 Ce + 0.1 Y	0.0036	0.0136	28	1466
DZ	Zr-2 + 0.1 Ce + 0.1 Y + 0.1 Au	0.0040	0.0127	26	1466
EA	Zr-4	0.0032	0.0043	8	1037
EB	Zr-4 + 0.1 Ce	0.0037	0.0055	9	1037
EC	Zr-4 + 0.1 Y	0.0036	0.0053	10.5	1037
ED	Zr-4 + 0.1 Ce + 0.1 Y	0.0036	0.0064	14	1037
EE	Zr-4 + 0.1 Ce + 0.1 Y + 0.1 Au	0.0035	0.0062	12.5	1037
FZ	Zirconium (Zr) Sponge	-	-	-	152*
GL	Zr + 0.01 Ga	0.0046	0.0065	14	1156
GM	Zr + 0.1 Ga	0.0053	0.0085	22	1156
GN	Zr + 1.0 Ga	0.0053	0.0235	-	1156
GR	Zr-2	0.0039	0.0073	22	1156
GO	Zr-2 + 0.01 Ga	0.0037	0.0075	22	1156
GP	Zr-2 + 0.1 Ga	0.0036	0.0073	20	1156

*Spalling occurred

4. DISCUSSION OF RESULTS

4.1 Tensile Tests

The results listed in Table 3 (page 6) show that, with one exception, additions of cerium and yttrium, separately or together, effect a significant increase in the ultimate tensile and yield strengths of crystal bar zirconium and Zircaloy-4. In the exception (melt EB) there is no increase in ultimate tensile strength although the yield strength is improved. Single additions of cerium or yttrium were as effective as combined additions in improving the tensile strength of crystal bar zirconium but the combined addition of cerium and yttrium was more effective in the case of Zircaloy-4. The effect of gold alone was not determined but it can be seen from Table 3 that an addition of 0.1% Au to the Zircaloy-2 and Zircaloy-4 containing 0.1% Ce and 0.1% Y (melts DZ and EE) resulted in an appreciable reduction in strength of the latter alloys.

There was an increase in the ultimate tensile and yield strengths with increasing additions of gallium to sponge zirconium, the improvement being quite substantial at 1.0% Ga. The elongation was practically unaffected except at 1.0% Ga, when there was a slight reduction. A similar pattern occurred for Zircaloy-2 except that in this case the effect of the gallium was not so marked, especially at the 0.01% level.

4.2 Corrosion Tests

The corrosion results plotted in Figures 1 and 2 (pages 8 and 9) and listed in Table 4 (page 11) show that while additions of 0.1% Ce and 0.1% Y, singly or combined, or 0.1% Ce, 0.1% Y and 0.1% Au generally reduced the corrosion resistance of Zircaloy-2 and Zircaloy-4, alloys of crystal bar zirconium with 0.1% Ce, 0.1% Y and 0.1% Au were much more seriously affected.

Figure 3 (page 10) and Table 4 show that additions of 0.01% and 0.10% Ga improved the corrosion resistance of sponge zirconium in steam, bearing in mind that specimens of sponge zirconium without gallium additions started to spall after 152 hr of testing. Samples of sponge zirconium alloyed with 0.01% Ga showed a weight gain of only 39 mg/dm^2 after 1156 hr of exposure, and this compares favourably with the weight gain of 60 mg/dm^2 for Zircaloy-2 after the same exposure time. The alloy containing 1.0% Ga showed poor corrosion resistance. Additions of 0.10% Ga to Zircaloy-2 improved the latter's weight gain at transition, but after transition there was little difference.

The time to transition was closely similar for all the gallium alloys (except Zr + 1.0% Ga) being in the range 840 to 1000 hr. The post-transition corrosion rates were about the same for Zircaloy-2 and the alloys containing gallium except for the Zr + 0.01% Ga, which exhibited a lower rate than the others.

The corrosion resistance of the zirconium plus gallium alloys decreased with increasing gallium content and, of the three compositions tested, the Zr + 0.01% Ga alloy gave the best results; this might be related to the limit of solid solubility of gallium in zirconium. The alloys containing 1.0% Ga proved to be hot short, indicating that gallium was present at the grain boundaries.

The slight difference between the corrosion plots of Zircaloy-2 in Figures 2 and 3 (pages 9 and 10) can be explained by the fact that the Zircaloy-2 of Figure 2 was alloyed in the tungsten-arc furnace using sponge zirconium, whereas the Zircaloy-2 of Figure 3 was prepared simply by melting a piece of Zircaloy-2 tubing in the same furnace; although the test specimens were prepared in the same fashion, the different origins of the materials would explain the slight differences in the corrosion data obtained.

4.3 Hydrogen Absorption

The results given in Table 5 (page 12) show that, in every case, additions of cerium and yttrium caused an increase in hydrogen absorption. This increase was most marked in the case of crystal bar zirconium and only slight for Zircaloy-4. The gold additions resulted in a marked drop in hydrogen absorbed by the crystal bar alloys but had little or no effect on the Zircaloy-2 and Zircaloy-4 alloys.

The hydrogen absorbed by the zirconium-gallium alloys increased with increasing gallium content, but additions of gallium to Zircaloy-2 had no effect on hydrogen pick-up.

The amount of hydrogen absorbed by zirconium alloys during corrosion is considered by Berry et al[2] to be influenced by the nature and amount of intermetallic inclusions, and it has been shown by Biefer et al[3] that nickel-free Zircaloy-2 exhibits less hydrogen pick-up than normal Zircaloy-2. Zircaloy-4 is essentially nickel-free Zircaloy-2, and it can be seen from Table 5 that the hydrogen absorption was much lower for the Zircaloy-4 base alloys than for the Zircaloy-2 base alloys.

The hydrogen contents before corrosion are generally higher than one would expect but the reason for this is not known.

5. CONCLUSIONS

(1) Additions of 0.1% Ce and 0.1% Y, separately or combined, improved the tensile strengths of crystal bar zirconium, and Zircaloy-4.

(2) An addition of 0.1% Au reduces the tensile strength of Zircaloy-2 and Zircaloy-4 alloys containing 0.1% Ce and 0.1% Y.

(3) Additions of gallium improve the tensile properties of sponge zirconium, the degree of improvement increasing as the gallium addition is increased up to 1.0%, which was the maximum addition investigated.

(4) Additions of up to 1.0% Ga improve the tensile properties of Zircaloy-2, but the improvement is not as marked as in the case of sponge zirconium.

(5) Zirconium and Zircaloy-2 are made hot-short by the addition of 1.0% Ga.

(6) Additions of 0.1% Ce and 0.1% Y, singly or combined, and 0.1% Ce, 0.1% Y and 0.1% Au, cause a slight lowering of the corrosion resistance of Zircaloy-2 and Zircaloy-4 in steam at 400°C (750°F) and 1500 psi.

(7) Additions of 0.01% and 0.10% Ga effect a large improvement in the corrosion resistance of sponge zirconium to steam at 400°C (750°F) and 1500 psi. The 0.01% Ga alloy has superior corrosion resistance to Zircaloy-2 after 1156 hr of exposure to steam.

(8) Addition of 0.1% Ce and 0.1% Y (singly or combined) to crystal bar zirconium, Zircaloy-2 or Zircaloy-4 causes an increase in hydrogen absorption.

(9) Addition of 0.1% Au to crystal bar zirconium containing 0.1% Ce and 0.1% Y causes a decrease in hydrogen absorption.

6. FUTURE WORK

The most interesting results arising from this investigation are the effect of gold in reducing hydrogen absorption and the improvement in corrosion resistance and tensile strength brought about by addition of gallium to zirconium. It is planned to carry out a fuller investigation of the effect of gold and gallium additions to zirconium and its alloys.

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