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ABSTRACT

Cold worked specimens of iodide zirconium, Zircaloy-2, iodide titanium, and A-55 titanium were tested in a high pressure recombiner loop in an attempt to duplicate anomalous results obtained in a prior recombiner loop. Hydrogen analyses and metallographic examinations were made on all specimens. The titanium materials and Zircaloy-2 picked up major amounts of hydrogen in the cell section. None of the materials tested showed appreciable hydrogen absorption in the recombiner section. Complete recrystallization occurred in all cell specimens while only Zircaloy-2, of the recombiner specimens, showed any degree of recrystallization. No explanation for this behavior can be given.

A summary of the data obtained in previous recombiner loops is compared with the results of this loop. Conclusions were based on the results of three recombiner loops.

Primarily because of the hydrogen absorption data obtained in all three recombiner loops, it is recommended that the zirconium and titanium materials tested not be used in environments similar to those encountered in high pressure recombiner loops.

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Introduction

Recrystallization anomalies observed in zirconium and titanium materials corrosion tested in a recombiner loop have been reported previously.^{1,2} Specimens of iodide zirconium, Zircaloy-2, iodide titanium, and A-55 titanium were prepared and tested in a recombiner loop operated under identical conditions to attempt to duplicate the results.³ The specimens tested were made from the same stock material used to prepare specimens for the first recombiner loop. All materials were cold worked 25 to 50% and the specimens were chemically polished. Specimens tested in the recombiner loop, where electrolytically generated H_2 and O_2 are catalytically recombined, were at 350 to 425°C in the recombiner section and at 230 to 240°C in the vapor flow of the cell section. Each specimen submitted for this test was of a size unique among the set so that the possibility of error in identification could be eliminated. After 90 hr of exposure in the loop, which was operated by the HRP Component Development Section, the specimens were returned to HRP Metallurgy. Half of each specimen was sent for hydrogen analysis. The other half was retained for metallographic examination.

Discussion of Results

The hydrogen analyses of the corroded specimens and controls are given in Table I. Hydrogen contents of specimens from other recombiner loops are included for comparison. Except for the iodide zirconium specimens in the recombiner section and the Zircaloy-2 specimens in the cell, the hydrogen contents are substantially the same as reported for the previous test.^{1,2} The recombiner specimens of iodide zirconium picked up essentially no hydrogen (< 20 ppm) in this recombiner loop, while 1600 and 8000 ppm were reported for this material in the recombiner sections of other recombiner loops operated under similar conditions.^{1,2,4} Zircaloy-2 specimens in the cell, however, absorbed five to six times as much hydrogen as in the recombiner loops mentioned previously. These differences in hydrogen pickup cannot be explained.

The iodide zirconium specimens exposed to the vapor flow of the cell showed complete recrystallization and considerable grain growth. The rough-textured second phase seen in the photomicrographs of the iodide zirconium cell specimens,

TABLE I
Hydrogen Contents of Recombiner Loop Specimens

	Hydrogen - ppm											
	Iodide Zr			Zircaloy-2			Iodide Ti			A-55 Ti		
	Present Loop	Ref. 1	Ref. 4	Present Loop	Ref. 1	Ref. 4	Present Loop	Ref. 1	Ref. 4	Present Loop	Ref. 1	Ref. 4
Control	18	18	80	13	13	60	120	120	92	25	25	27
Cell-Vapor	71 ¹ 57	37	30	480 ¹ 350	71	78	1000 ¹ 1500	1200	120	540 ¹ 470	290	51
Cell-Liquid	--	--	28	--	--	63	--	--	1800	--	--	1100
Recombiner	40 ¹ 32	1600	8000	32	23	140	100 ¹ 100	120	140	33 ¹ 32	33	70

1. Duplicate loop specimens.

Figs. 1a and 1b, has been identified by anodization techniques⁵ as hydride. The photomicrographs of the cell specimens were selected to show areas containing the hydride phase and are not truly representative of the amount of hydride present (60 to 70 ppm hydrogen). There are areas many times the size of those shown in the figures with no hydride present. The needle-like objects seen in these same photomicrographs, very evident in Fig. 1b, are twins. No recrystallization occurred in the recombiner specimens, Figs. 1c and 1d, although they were at temperatures 100 to 200°C higher than the cell specimens. Less than 20 ppm hydrogen was picked up by these specimens. As noted previously, iodide zirconium specimens in the recombiner sections of two other recombiner loops^{1,4} absorbed 1600 and 8000 ppm hydrogen.

Definite conclusions regarding the recrystallization of iodide zirconium in the recombiner sections of these two loops cannot be made since the starting material in one was not cold worked¹ and because metallographic preparation of the specimen from the other⁴ was impossible due to the extremely high hydrogen content. It is not known, then, whether the lack of recrystallization in this loop is in any way related to the low hydrogen pickup.

Zircaloy-2 specimens exposed in the cell section completely recrystallized and picked up 400 ppm hydrogen. Complete recrystallization of Zircaloy-2 cell specimens has been noted previously,^{1,4} but with about one-sixth the hydrogen pickup. The hydride phase appears as platelets, Figs. 2a and 2b, in the Zircaloy-2 grain boundaries. Fe, Ni, and Cr intermetallics are also seen in the grain boundaries, but as dot-type precipitates. Partial recrystallization occurred in the Zircaloy-2 recombiner specimen, Fig. 2c. The second phase present is the intermetallic mentioned above. Hydrogen pickup was < 20 ppm.

The two iodide titanium cell specimens showed complete recrystallization, grain growth, and hydrogen pickups of 900 and 1400 ppm, respectively. The massive islands of second phase seen in the microstructures of the iodide titanium cell specimens, Figs. 3a and 3b, are hydrides. Apparently no recrystallization has occurred in the recombiner specimens, Figs. 3c and 3d. No hydrogen was absorbed by either of the specimens.

A-55 titanium specimens in the cell of the recombiner loop, Figs. 4a and 4b, picked up approximately 500 ppm hydrogen and were completely recrystallized.

BRIGHT FIELD

POLARIZED LIGHT

(a) RL-9 CELL (57 ppm H_2)

(b) RL-13 CELL (71 ppm H_2)

(c) CL-9 RECOMBINER (40 ppm H_2)

(d) CL-13 RECOMBINER (32 ppm H_2)

Fig. 1. Iodide Zirconium. 500X. Reduced 34%.

BRIGHT FIELD

POLARIZED LIGHT

(a) RL-8 CELL (350 ppm H_2)

(b) RL-12 CELL (480 ppm H_2)

(c) CL-12 RECOMBINER (32 ppm H_2)

Fig. 2. Zircaloy-2. 500X. Reduced 33%.

BRIGHT FIELD

POLARIZED LIGHT

(a) RL-7 CELL (1000 ppm H_2)

(b) RL-11 CELL (1500 ppm H_2)

(c) CL-7 RECOMBINER (100 ppm H_2)

(d) CL-11 RECOMBINER (100 ppm H_2)

Fig. 3. Iodide Titanium. 500X. Reduced 34%.

BRIGHT FIELD

POLARIZED LIGHT

(a) RL-6 CELL (470 ppm H_2)

(b) RL-10 CELL (540 ppm H_2)

(c) CL-6 RECOMBINER (32 ppm H_2)

(d) CL-10 RECOMBINER (33 ppm H_2)

Fig. 4. A-55 Titanium. 500X. Reduced 34%.

The hydrides are seen as platelets in the grain boundaries and as very small islands in the grains. As in the case of the iodide titanium, no recrystallization occurred in the recombiner specimens, Figs. 4c and 4d. Likewise, no hydrogen was absorbed.

In this recombiner loop and in those reported previously^{1,4} iodide zirconium, Zircaloy-2, iodide titanium, and A-55 titanium have invariably recrystallized in the cell sections, with or without hydrogen absorption, while the same materials in the recombiner section may or may not recrystallize, and in no orderly fashion. Times and recombiner temperatures of the three loops under discussion are:

1. 350-425°C for 90 hr - present loop,
2. 350-425°C for 188 hr,¹
3. 430-500°C for 336 hr.⁴

The titanium specimens in the recombiner sections showed no recrystallization in 90 hr, partial recrystallization in 188 hr, and complete recrystallization in 336 hr. It should be noted, however, that the 336 hr specimens were at a temperature ~ 100°C higher than the 90 and 188 hr specimens. Iodide and A-55 titanium, then, seem to show a time-temperature recrystallization dependence in the recombiner sections. Little or no hydrogen was absorbed by any of the specimens.

In the case of Zircaloy-2, partial recrystallization is shown by the recombiner specimens in all three loops. Due to the differences in the condition of starting material and the extremely high hydrogen contents for some specimens, mentioned previously, no recrystallization sequence can be given for iodide zirconium.

A summary of the structural changes observed in specimens exposed in recombiner loops and the operating conditions for each of these loops is given in Tables II and III.

No matter how one may rationalize the degrees of recrystallization in the recombiner specimens, there remains the problem of explanation of the recrystallization of the cell specimens, held at temperatures well below their normal recrystallization temperatures, while no or only partial recrystallization occurred in the corresponding recombiner specimens held at a higher temperature. No correlation between this behavior and hydrogen absorption or total corrosion has

TABLE II

Summary of Structural Changes Observed in Zirconium and Titanium Specimens Exposed in Recombiner Loops

Material	Loop Identity	Description of Specimen	
		Cell Section	Recombiner Section
Iodide Zirconium	Present Loop	Complete recrystallization and considerable grain growth. Hydride present.	No recrystallization.
Iodide Zirconium	Ref. 1	Original material was not cold worked. Grain growth occurred.	Some grain growth. Much hydride present.
Iodide Zirconium	Ref. 4	Complete recrystallization and some grain growth. Hydride present. (For both cell-liquid and cell-vapor specimens)	Metallographic preparation impossible due to high hydrogen content.
Zircaloy-2	Present Loop	Complete recrystallization. Hydride platelets in grain boundaries.	Partial recrystallization.
Zircaloy-2	Ref. 1	Complete recrystallization. Hydride platelets in grain boundaries.	Partial recrystallization.
Zircaloy-2	Ref. 4	Partial recrystallization in cell-liquid and in cell-vapor specimens.	Partial recrystallization, but less than in either cell section.
Iodide Titanium	Present Loop	Complete recrystallization, grain growth, and massive islands of hydride.	No recrystallization.
Iodide Titanium	Ref. 1	Complete recrystallization, grain growth, and massive hydrides.	Partial recrystallization. Hydrides in grain boundaries.
Iodide Titanium	Ref. 4	Complete recrystallization in both cell-liquid and cell-vapor. Many hydrides in cell-liquid sample, fewer hydride platelets in cell-vapor sample.	Complete recrystallization. Hydride platelets.
A-55 Titanium	Present Loop	Complete recrystallization. Hydride platelets in grain boundaries and hydride islands in grains.	No recrystallization.
A-55 Titanium	Ref. 1	Complete recrystallization, grain growth. Hydrides in grain boundaries.	Partial recrystallization.
A-55 Titanium	Ref. 4	Complete recrystallization in both cell-liquid and cell-vapor samples. Many hydride platelets in cell-liquid specimen, very few in cell-vapor specimen.	Complete recrystallization. A few grain boundary platelets of hydride.

TABLE III

Summary of Exposure Conditions in Recombiner Loops

Recombiner Loop	Time in Operation hr.	Pressure psi	Temperature - °C		
			Cell-Vapor ¹	Cell-Liquid ²	Recombiner ³
Present Loop	90	~500	230-240	-- ⁴	350-425
Ref. 1	188	~500	230-240	-- ⁴	350-425
Ref. 4	336	575-600	235-280	230	430-500

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1. Superheated steam, H_2 and O_2 , entrained caustic, and probable contact with foaming caustic.
2. KOH- H_2O solution containing dissolved H_2 and O_2 .
3. Superheated steam, H_2 and O_2 , possible limited contact with KOH.
4. No specimens exposed.

been found. A more basic study would be necessary to determine the cause of the observed low-temperature recrystallization and the difference in behavior between zirconium and titanium which normally react in a similar fashion with hydrogen and exhibit similar recrystallization characteristics.

It is important to realize that exposure conditions in the recombiner loops involve contact with a KOH solution and vapor containing entrained KOH. The behavior of the materials tested in this and other recombiner loops^{1,4} cannot then be extrapolated to predict their behavior in the highly oxidizing environments encountered in HRP fuel solutions.

Conclusions and Recommendations*

Complete recrystallization of iodide zirconium, Zircaloy-2, iodide titanium, and A-55 titanium occurred in the cell section of the recombiner loop at temperatures considerably below their normal recrystallization temperatures. The degree of recrystallization of iodide titanium and A-55 titanium in the recombiner section appeared to be a function of time and temperature. It is suspected, although not certain, that this same relationship holds for iodide zirconium and Zircaloy-2.

Iodide titanium and A-55 titanium absorbed major amounts of hydrogen when exposed to the environment of the recombiner loop cell section. Essentially no hydrogen was picked up by these same materials in the recombiner section. Hydrogen pickup for iodide zirconium in the recombiner section has been appreciable in other recombiner loops but was negligible in this loop. Minor amounts of hydrogen were absorbed by iodide zirconium in the cell section. Large amounts of hydrogen were absorbed by the Zircaloy-2 cell specimens in this loop, while hydrogen pickup in previously reported recombiner loops was much less. Small amounts of hydrogen were absorbed by the Zircaloy-2 recombiner section specimens. Inconsistencies in the amounts of hydrogen absorbed point out that there must be an uncontrolled and unknown variable influencing hydrogen pickup.

* The conclusions and recommendations made here apply equally well to the recombiner loops previously reported.^{1,4}

Use of the materials tested in this loop in environmental conditions similar to those of the test is not recommended. Enough hydrogen was picked up in most cases to cause serious embrittlement and possible catastrophic failure.

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