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ABSTRACT

Specimens of iodide zirconium, Zircaloy-2, Zr-15Nb, iodide titanium, TMCA-45 titanium, A-110AT titanium, and 430 stainless steel were corroded in a High Pressure Recombiner Loop. Analyses were performed to determine the amount of hydrogen pickup. The titanium materials and iodide zirconium showed very high hydrogen pickups, while the zirconium alloys and the 430 stainless steel absorbed smaller amounts of hydrogen. Metallographic examination of the specimens showed that recrystallization occurred in all but the Zr-15Nb specimens. There seems to be little difference in the extent of recrystallization and grain growth whether the specimens were in the boiler section at 230 to 280°C or in the recombinder section at 430 to 500°C. Recrystallization of the boiler samples cannot, at present, be explained or correlated in any way with the amount of hydrogen absorption. Similarly, the amount of hydrogen absorbed cannot be correlated to the amount of corrosion that occurred.

Since hydrogen is known to seriously embrittle zirconium and titanium, it is recommended that crystal-bar zirconium and titanium alloys not be used as materials of construction in environments similar to that of the High Pressure Recombiner Loop.

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INTRODUCTION

Duplicate specimens of iodide zirconium, Zircaloy-2, Zr-15Nb, iodide titanium, TMCA-45 titanium, and A-110AT titanium were prepared and submitted to the Component Development Section for corrosion testing in the High Pressure Recombiner Loop. All of the materials were either cold or warm rolled to a reduction of 40 to 60 per cent. In addition to the materials supplied by HRP Metallurgy, specimens of a modified 430 stainless steel were exposed.

The High Pressure Recombiner Loop, in which electrolytically generated H_2 and O_2 are catalytically recombined, was operated by the Component Development Section for a total of 310 continuous hours at full temperature and a pressure of 575 to 600 psi.¹ Specimens were tested in three positions in the Recombiner Loop; in the liquid and vapor sections of the boiler and in the recombiner.

The exposure conditions as reported by B. A. Hannaford² and the specimen code are given below:

1. Boiler Liquid Samples. AL and BL. A 15 to 20% KOH solution containing dissolved H_2 and O_2 . Chloride < 2 ppm. Temperature 230°C.
2. Boiler Vapor Samples. AV and BV. Superheated steam, ~ 5% stoichiometric $H_2 + 1/2 O_2$. Also probable contact with foaming caustic. Temperature 235-280°C.
3. Recombiner Samples. AR and BR. Superheated steam, ~ 1-1.3% stoichiometric $H_2 + 1/2 O_2$. Possible limited contact with KOH. Temperature normally 430-500°C, as high as 600°C for approximately one hour.

Specimens labeled AC and BC were controls and received no exposure. After exposure the duplicate sets of specimens were returned to the HRP Metallurgy Section for disassembly and examination. The 'B' specimens were sectioned; one part was sent for hydrogen analysis by equilibrium pressure and the other part was mounted for metallographic examination. The 'A' set of specimens was returned for further exposure.

DISCUSSION OF RESULTS

Figures 1 and 2 show the High Pressure Recombiner Loop specimens before and after disassembly. Although not readily apparent in either macrograph, appreciable corrosion was shown by all of the titanium materials and the 430 stainless steel in both the liquid and vapor sections of the boiler. Zirconium specimens, except for iodide zirconium in the recombiner section, showed no measurable corrosion and little hydrogen pickup. Corrosion data, as change in thickness, is presented in Table I. Weight-loss data could not be obtained without damaging the specimens during removal of the tenacious oxides on some specimens and because of spalling losses on others.

The hydrogen analyses of the exposed specimens and of the controls are given in Table II. Comparison of the data with that obtained in prior loops^{3,4} shows several discrepancies in the hydrogen contents for a given material in a particular position. Metallographic examination of the specimens confirmed generally the hydrogen contents determined by analysis. Attempts to correlate hydrogen contents with the amount of corrosion that occurred were made, but with negative results. This was not too unexpected since correlation of hydrogen in Zircaloy-2 with the amount of corrosion has been difficult even in controlled laboratory tests.

The structures of the iodide zirconium specimens are shown in Fig. 3. The original material, 1BC, was cold rolled 40%. Complete recrystallization occurred in the specimens held in the liquid and vapor sections of the boiler, Figs. 3b and 3c. Anodization techniques⁵ have shown that the second phase is hydride, and that the needle shaped platelets which are seen in many of the grains are twins. The apparent loss of hydrogen in both of these samples is probably explained by hydrogen segregation in the starting material. Specimen 1BR, held in the recombiner section, picked up 8000 ppm hydrogen. Figure 3d shows the specimen as mechanically polished, as attempts to show the microstructure by ordinary methods failed. The dark areas are oxide which has consumed over half of the original material by an attack which seems to be primarily intergranular.

Fig. 1 (Y-24981) Specimen Arrays as Removed from Recombiner Loop. From lower left to upper right, Cell Vapor Section, Recombiner Section, Cell Liquid Section.

HIGH PRESSURE RECOMBINER LOOP-310 hrs EXPOSURE

Fig. 2 (Y-24951) Recombiner Loop Specimens after Disassembly from Arrays.

TABLE I

CORROSION OF RECOMBINER LOOP SPECIMENS

<u>Specimen Position</u>	<u>Thickness Change - mils</u>						
	<u>Iodide Zr</u>	<u>Zircaloy-2</u>	<u>Zr-15Nb</u>	<u>Iodide Ti</u>	<u>TMCA-45 Ti</u>	<u>A-110AT Ti</u>	<u>430 Stainless Steel</u>
Cell Liquid (230°C)	0	0	0	-15	-12	-23	-16
Cell Vapor (235-280°C)	0	0	0	-11	-8	-23	-9
Recombiner (430-500°C)	-42	0	0	0	-5	0	0

TABLE II

HYDROGEN CONTENTS OF RECOMBINER LOOP SPECIMENS

<u>Specimen Position</u>	<u>Hydrogen - ppm</u>						<u>430 Stainless Steel</u>
	<u>Iodide Zr</u>	<u>Zircaloy-2</u>	<u>Zr-15Nb</u>	<u>Iodide Ti</u>	<u>TMCA-45 Ti</u>	<u>A-110AT Ti</u>	
Control	80	60	44	92	27	73	4
Cell Liquid (230°C)	28	63	46	1800	1100	4500 ^f	47
Cell Vapor (235-280°C)	30	78 ^b	62	120 ^d	51 ^e	1400	14
Recombiner (430-500°C)	8000 ^{a,f}	140 ^c	90	140	70	190	9

a. 1600, 40-32 on prior runs

b. 71, 480-350 on prior runs

c. 23, 32-33 on prior runs

d. 1200, 1000-1500 on prior runs

e. 290, 470-540 on prior runs

f. Estimated - pressure too high for accurate reading in analysis

BRIGHT FIELD

Y-25621

Y-25625

Y-25623

BRIGHT FIELD 100X

Y-26079

POLARIZED LIGHT

Y-25620

Y-25624

Y-25622

BRIGHT FIELD

Y-26080

(a) 1BC CONTROL
80 ppm H_2

(b) 1BL BOILER LIQUID
28 ppm H_2

(c) 1BV BOILER VAPOR
30 ppm H_2

(d) 1BR RECOMBINER
8000 ppm H_2

Fig. 3. Iodide Zirconium, 500X Except Where Noted. Reduced 55% in Reproduction.

The microstructure of the starting material for the Zircaloy-2 specimens, rolled 50% at 480°C, is shown in Fig. 4a. Complete recrystallization did not occur in any of the Zircaloy-2 specimens. All of the specimens did, however, recrystallize to some extent. The specimen exposed to the boiler liquid, 2BL, exhibited the most recrystallization and picked up essentially no hydrogen. Specimens in the boiler vapor and the recombiner sections, 2BV and 2BR, Figs. 4c and 4d, recrystallized to somewhat lesser extents although they were at higher temperatures, more than 200°C higher in the case of the recombiner specimen. The recombiner specimen, 2BR, was the only Zircaloy-2 specimen to pick up any appreciable amount of hydrogen (80 ppm). In a previous loop,³ the Zircaloy-2 specimen in the boiler vapor was completely recrystallized, while that in the recombiner section showed essentially no recrystallization and no hydrogen pickup. Identification of hydrides in this material is difficult due to low hydrogen content, the worked structure, and the high stringer content.

The structures of the Zr-15Nb alloy samples, Fig. 5, are essentially identical. The starting stock was finished to size by a cold reduction of 50% and apparently no recrystallization occurred in any of the exposed specimens. Although analyses showed hydrogen contents up to 90 ppm in the case of the recombiner specimen, hydride identification was impossible due to the worked structure and the presence of retained beta phase (bcc) which has a high solubility for hydrogen.

All of the iodide titanium specimens exposed to the loop environment completely recrystallized. A microstructure of the original material, cold rolled 50%, is shown in Fig. 6a. Specimen 4BL, held in the boiler liquid, had a hydrogen pickup of 1700 ppm, while the specimens in the boiler vapor and recombiner sections, 4BV and 4BR respectively, picked up only a fraction of this amount. Both the platelets and the particles shown in the microstructures of the iodide titanium, Figs. 6b, 6c, and 6d, are most certainly hydrides; those seen in Fig. 6a are due to an etching effect on the severely worked structure.

The structures of the TMCA-45 titanium show the same progression as that of the iodide titanium. Reduction of the starting material was again 50%, and recrystallization occurred in all of three of the exposed specimens. The

BRIGHT FIELD

Y-26086

Y-25629

Y-25627

Y-25631

POLARIZED LIGHT

Y-26085

Y-25628

Y-25626

Y-25630

(a) 2BC CONTROL
60 ppm H_2

(b) 2BL BOILER LIQUID
63 ppm H_2

(c) 2BV BOILER VAPOR
78 ppm H_2

(d) 2BR RECOMBINER
140 ppm H_2

Fig. 4. Zircaloy-2, 500X. Reduced 56% in Reproduction.

BRIGHT FIELD

Y-25938

Y-25942

Y-25940

Y-25944

POLARIZED LIGHT

Y-25937

Y-25941

Y-25939

Y-25943

(a) 3BC CONTROL
44 ppm H_2

(b) 3BL BOILER LIQUID
46 ppm H_2

(c) 3BV BOILER VAPOR
62 ppm H_2

(d) 3BR RECOMBINER
90 ppm H_2

Fig. 5. Zr-15Nb, 500X. Reduced 56% in Reproduction.

BRIGHT FIELD

Y-25633

Y-26082

Y-25635

Y-25637

POLARIZED LIGHT

Y-25632

Y-26081

Y-25634

Y-25636

(a) 4BC CONTROL
92 ppm H_2

(b) 4BL BOILER LIQUID
1800 ppm H_2

(c) 4BV BOILER VAPOR
120 ppm H_2

(d) 4BR RECOMBINER
140 ppm H_2

Fig. 6. Iodide Titanium, 500X. Reduced 56% in Reproduction.

specimen tested in the boiler liquid, 5BL, picked up 1100 ppm hydrogen, which appears as the grain boundary platelets in Fig. 7b. Smaller amounts of hydrogen were picked up by the recombiner and the boiler vapor specimens. The few grain boundary platelets appearing in the microstructures of these specimens, Figs. 7c and 7d, are probably hydrides, while the small islands in the grains are retained beta.

The alpha titanium alloy, A-110AT, rolled 40% at 600°C before testing, showed a high hydrogen pickup in both the vapor stream and the liquid of the boiler, 1300 and 4400 ppm, respectively. Figure 8 shows that no large amount of recrystallization has occurred in any of the specimens, the major difference in microstructure (seen in both 6BL and 6BV) being the hydride platelets in the grain boundaries. It is questionable whether the grain boundary phase in 6BC and 6BR, Figs. 8a and 8d, is entirely a hydride or is a Ti-Al-Sn intermetallic.

The microstructures of the modified 430 stainless steel specimens are shown in Fig. 9. Discounting metallographic effects, there seem to be no considerable differences in structure in any of the specimens. All of the specimens picked up some hydrogen, but the importance of this pickup cannot be readily evaluated because of the lack of knowledge of the effects of hydrogen in 430 stainless steel.

In a 188-hr recombiner loop reported previously,³ recrystallization and considerable grain growth occurred in the boiler section specimens of iodide zirconium, Zircaloy-2, A-55 titanium, and iodide titanium, while the same materials in the recombiner section recrystallized to a considerably lesser extent. The hydrogen pickup data for the 188-hr loop are presented in the footnotes of Table II. Examination of these same materials from the present loop shows that there seems to be little or no difference in the extent of recrystallization and growth in boiler and recombiner. It should be noted, however, that while the recombiner temperature in the 188-hr loop was 350 to 425°C the temperature in this loop was 430 to 500°C, and as high as 600°C for approximately one hour. These times and temperatures are sufficient to allow the recrystallization noted in the recombiner specimens. No explanation can at this time be given for the anomalous behavior of the boiler specimens.

BRIGHT FIELD

Y-25641

Y-25643

Y-25639

Y-25645

POLARIZED LIGHT

Y-25640

(a) 5BC CONTROL
27 ppm H_2

Y-25642

(b) 5BL BOILER LIQUID
1100 ppm H_2

Y-25638

(c) 5BV BOILER VAPOR
54 ppm H_2

Y-25644

(d) 5BR RECOMBINER
70 ppm H_2

Fig. 7. TMCA-45 Titanium, 500X. Reduced 56% in Reproduction.

BRIGHT FIELD

Y-25647

Y-26084

Y-25649

Y-25946

POLARIZED LIGHT

Y-25646

Y-26083

Y-25648

Y-25945

(a) 6BC CONTROL
73 ppm H_2

(b) 6BL BOILER LIQUID
4500 ppm H_2

(c) 6BV BOILER VAPOR
1400 ppm H_2

(d) 6BR RECOMBINER
190 ppm H_2

Fig. 8. A-110AT Titanium, 500X. Reduced 56% in Reproduction.

Y-25933

(a) 7BC CONTROL
4 ppm H_2

Y-25935

(b) 7BL BOILER LIQUID
47 ppm H_2

Y-25934

(c) 7BV BOILER VAPOR
14 ppm H_2

Y-25936

(d) 7BR RECOMBINER
9 ppm H_2

As before, it is impossible to explain the recrystallization of the zirconium and titanium materials at temperatures as low as 230 to 280°C. It does not seem to be directly related to the hydrogen absorption, since recrystallization occurred at these temperatures in some cases with no hydrogen pickup.

Since zirconium and titanium alloys are known to react in similar fashions with hydrogen, no explanation can be given for their differences in behavior under the reported conditions.

It should be emphasized that the exposure conditions for the specimens tested in this loop involve KOH entrainment in the vapor and a 15 to 20% KOH solution in the boiler. These conditions are drastically different from the highly oxidizing environments that would be encountered in HRP fuels.

CONCLUSIONS AND RECOMMENDATIONS

Iodide titanium and titanium alloys pick up major amounts of hydrogen and exhibit considerable corrosion when exposed to the environment of the Recombiner Loop boiler. Smaller amounts of hydrogen are absorbed by titanium materials in the recombiner section. Iodide zirconium and zirconium alloys absorb more hydrogen in the recombiner than in the boiler section. Enough hydrogen is picked up in the case of iodide zirconium and the titanium materials, either in the boiler, the recombiner, or both, to cause serious embrittlement. Embrittlement of the zirconium alloys would probably be much less serious, but still damaging.

On the basis of the observations made above, it is recommended that iodide zirconium, and titanium alloys, not be used as constructional materials in environments of the type encountered in the High Pressure Recombiner Loop. Recommendations as to the use of zirconium alloys would be speculative.

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