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SUBJECT: Examination of Recombiner Loop
Specimens of Zr and Ti Alloys

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SUMMARY

Specimens of A-55 Ti, Ti-6Al-4V, crystal bar Ti, crystal bar Zr, and Zircaloy-2 were corroded in a recombiner loop. The specimens were analyzed for hydrogen pickup and examined metallographically. All specimens showed some hydrogen pickup, with crystal bar Zr and Ti showing a very large pickup of hydrogen. All alloys, except the Ti-6Al-4V, showed evidence of recrystallization and grain growth in the cell section and only recrystallization in the recombiner section although it was operated at a higher nominal temperature. These effects cannot be explained at the present.

It is recommended that the recombiner loop experiment be repeated, with particular care being taken in identification of the specimens, to see if the results can be reproduced. Critical experiments in a hydrogen charging apparatus are scheduled to determine the possibility of causing the recrystallization and grain growth out of the loop under very carefully controlled conditions.

It is also recommended that the commercial sponge Ti alloys, A-55, A-40, etc. not be used as a constructional material for the loops until a more complete check on the hydrogen pickup is made, since it has been shown that titanium is easily embrittled by a relatively small amount of hydrogen, and the commercial limit of fabricated bar and plate Ti has been placed at 150 ppm hydrogen.

INTRODUCTION

Specimens of A-55 Ti, Ti-6Al-4V, crystal bar Ti, crystal bar Zr, and Zircaloy-2 were prepared and submitted for corrosion testing in the recombiner loop where electrolytically generated H₂ and O₂ were catalytically recombined. As was reported to me, the loop was operated for a total of 188 hr with several shut-downs during that period, the specimens labeled RL were held in the vapor flow of the recombiner section at a temperature of 350° to 425°C, and the specimens labeled CL were held in the vapor of the cell

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section at a temperature of 230° to 240°C. The specimens labeled RL - C were control specimens which did not receive any exposure. After corrosion and receipt of the specimens, they were sectioned with one part submitted for hydrogen analysis by vacuum fusion and the other part mounted for metallographic examination.

RESULTS

The hydrogen analyses of the corroded specimens and of the controls are given in Table I. Micrographs of the specimens are given in Figures 1 through 30.

Metallographic examination confirmed approximately, in all cases, the hydrogen contents determined by vacuum fusion analysis. No exact hydrogen analysis by metallographic means can be made, since I have no data correlating hydrogen content to volume per cent hydride present in the microstructure.

DISCUSSION OF RESULTS

The structures of the Ti-6Al-4V specimens are not appreciably different. In comparison with structures shown in the literature, those structures shown in Figures 1 through 6 are typical and representative of the alloy. It is possible that the apparent hydrogen pickup shown by the data was not true and that the differences in hydrogen content were due to a hydrogen segregation in the alloy bolt from which the specimens were cut. This is shown by the control specimen having a higher hydrogen content than the recombiner specimen.

The structures of the A-55 titanium specimens do show a great deal of difference and a progression of structures that, at the present time, cannot be explained. The original material was cold worked, as shown by the structure of the control specimen, Figures 7 and 8. The hydrogen content difference shown by the control and the recombiner specimens is within the range of analyses on any one sheet although these specimens were cut side by side from the sheet stock. The specimen in the recombiner section, RL-5, Figures 9 and 10,

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underwent some recrystallization (just started). However, the specimen held in the cell section, CL-5, Figures 11 and 12, at 230° to 240°C, underwent complete recrystallization with considerable grain growth, at a temperature far below its normal recrystallization temperature of 550° to 600°C. Numerous hydride platelets can be seen in the grain boundaries. It is believed that all of the plate-like second phase shown in the microstructures of RL-5 and CL-5 is hydride with the retained beta phase appearing as the more massive islands. The recrystallization occurring in CL-5 would be completely unexpected at the given operating temperature range and is inexplicable at the present.

The structures of the crystal bar titanium specimens show the same progression as those of the A-55 titanium specimens, with the hydrogen pickup, recrystallization, and grain growth of the cell specimen being much more extensive. The dark structures as well as the platelets in the grain boundaries of the microstructures of Figures 13 through 18 are definitely hydrides. The grain size of specimen CL-4 is quite large, being on the order of ASTM No. 1 or larger. The recrystallization occurring in the recombiner specimen, RL-2, Figures 15 and 16, is more extensive than that of the A-55 specimen, RL-5, as would be expected from the A-55 structure, since the crystal bar material is much purer and would be expected to undergo complete recrystallization at a temperature lower than the sponge material, A-55.

The structures of the Zircaloy-2 specimens show the same progression as the titanium specimens. The original material was cold worked, as shown by the control specimen, RL-4C, Figures 19 and 20. The specimen held in the recombiner, RL-4, Figures 21 and 22, has undergone partial recrystallization with no appreciable hydrogen pickup. The differences in the stringer contents of the recombiner specimen, RL-4, and the control specimen, RL-4C, shown in Figures 19 through 22, is not unusual in fabricated Zircaloy-2 plate, even in specimens cut from the same small piece of stock. It is not believed that

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this difference is significant. The cell specimen, CL-2, Figures 23 and 24, underwent complete recrystallization and has the appearance of material which has been fully annealed at approximately 700°C and containing approximately 100 ppm H₂. The plate-like phase appearing in the grain boundaries of Figure 23 is definitely hydride, identified by the anodizing technique we use, and the small, faint, dot precipitates appearing primarily in the grain boundaries are the Fe, Ni, and Cr intermetallics with Zr.

The structures of the crystal bar zirconium specimens are shown in Figures 25 through 30, and are not unexpected in the light of the structures shown by the other specimens. The original material was not cold worked, although there is evidence, in Figures 25 through 28, that a small amount of cold work is present, (probably less than 5%), as shown by the twins present in the structures. The recombiner specimen picked a very considerable amount of hydrogen, 1600 ppm, while the cell specimen did not pick up any appreciable amount, the reverse of the case for the crystal bar titanium specimens. The second phase shown in the micrographs of Figures 25 through 30 is, in all cases, definitely hydride, having been identified by our anodizing technique.

The recrystallization and grain growth of all of the cell specimens, occurring at the temperature reported, is completely unexpected and inexplicable. I can postulate several possibilities for the explanations but these need to be thoroughly checked, both by critical controlled experiments out of the loop and by a rerun of the loop to see if the structures can be duplicated in a second run.

If it is assumed that the process of the absorption of hydrogen appreciably lowers the activation energy for recrystallization then it is possible to grudgingly admit the vague possibility of recrystallization occurring even for the A-55 titanium specimen, at or near 240°C. It does not explain, however, the fact that the recombiner specimens, operating at

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a higher temperature, recrystallized to a considerably lesser extent and picked up only a small amount of hydrogen.

If it is assumed that there is a possibility of mix-up in the specimens, in that the specimens listed as being in the cell section were actually in the recombiner section, and vice versa, more order can be made out of the structures and a more feasible explanation can be made for the titanium specimens, but not for the zirconium specimens. This explanation is as follows: for the titanium specimens, the temperature of operation of the recombiner section is within the temperature range of the alpha plus beta structure for the Ti-H alloy system. With several shut-downs of the system during the time of exposure for the specimens, the specimens would have been cycled from a temperature range where the structure of alpha titanium plus hydride was stable, to a temperature range where the structure of alpha plus beta titanium was stable. Since a phase change would be occurring, that is, hydride to beta titanium, recrystallization and grain growth could take place with great ease at a temperature much lower than the normal recrystallization temperature for cold worked alpha titanium. This explanation does not fit for the zirconium specimens since the greatest pickup of hydrogen occurred in the specimen having no grain growth as well as the fact that the lowest temperature at which zirconium could show an alpha plus beta Zr structure is 575°C.

Particular care was taken in numbering the specimens as they were removed from the envelopes in which they were contained when received from the corrosion test. The specimens were removed and marked by me to insure that no possible mix-up could occur. Several specimens were broken out of the metallographic mounts to determine that they were not incorrectly labeled after mounting. Herschel Davis, Analytical Chemistry Division, who performed the vacuum fusion analyses, was asked to and did take particular care that the specimens were not mixed up. That any mix-up occurred after the specimens

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were removed from their original envelopes and marked is shown to be unlikely by the consistent order of the analyses and microstructures.

It is quite possible that no mix-up occurred at any time and that the analyses and structures found are true. If this is so, a very intriguing and fundamental concept for the evaluation and examination of recrystallization mechanisms and theory has been found.

A set of controlled and critical experiments are being scheduled in the hydrogen absorption apparatus to determine if recrystallization of cold worked crystal bar Ti and Zr is possible in the temperature range of 200° to 400°C in a hydrogen atmosphere.

Would it be possible in the near future to run a new set of specimens in a recombiner loop to attempt to duplicate the results reported herein?

It is recommended that A-55, A-40, A75, etc., not be used as constructional materials for loops until these experiments have been repeated and the results evaluated. Hydrogen contamination has been shown to seriously embrittle titanium and the commercial limit on Ti plate has been placed at 150 ppm H₂ due to such embrittlement.

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TABLE I

Hydrogen Contents of Recombiner Loop Corrosion Specimens

<u>Alloy</u>	<u>Recombiner</u>		<u>Cell</u>		<u>Control</u>	
	<u>Spec. No.</u>	<u>H₂ (ppm)</u>	<u>Spec. No.</u>	<u>H₂ (ppm)</u>	<u>Spec. No.</u>	<u>H₂ (ppm)</u>
Ti-6Al-4V	RL-1	73	CL-3	230	RL-1C	140
A-55 Ti	RL-5	33	CL-5	290	RL-5C	25
X-bar Ti	RL-2	120	CL-4	1200	RL-2C	120
X-bar Zr	RL-3	1600	CL-1	37	RL-3C	18
Zr-2	RL-4	23	CL-2	71	RL-4C	13

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Bright Field

Polarized Light

Control

Fig. 1. RL-1C 140 ppm H₂ (Y19394)

Fig. 2. RL-1C 140 ppm H₂ (Y19395)

Recombiner

Fig. 3. RL-1 73 ppm H₂ (Y19396)

Fig. 4. RL-1 73 ppm H₂ (Y19397)

Cell

Fig. 5. CL-3 230 ppm H₂ (Y19398)

Fig. 6. CL-3 230 ppm H₂ (Y19399)

Ti-6Al-4V

500X

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Polarized Light

Control

Fig. 7. RL-5C 25 ppm H₂ (Y19418)

Fig. 8. RL-5C 25 ppm H₂ (Y19419)

Recombiner

Fig. 9. RL-5 33 ppm H₂ (Y19422)

Fig. 10. RL-5 33 ppm H₂ (Y19423)

Cell

Fig. 11. CL-5 290 ppm H₂ (Y19420)

Fig. 12. CL-5 290 ppm H₂ (Y19421)

A-55 Ti.

500X

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Polarized Light

Fig. 13. RL-2C 120 ppm H₂ (Y19400)

Control

Fig. 14. RL-2C 120 ppm H₂ (Y19401)

Fig. 15. RL-2 120 ppm H₂ (Y19402)

Recombiner

Fig. 16. RL-2 120 ppm H₂ (Y19403)

Fig. 17. CL-4 1200 ppm H₂ (Y19404)

Cell

Fig. 18. CL-4 1200 ppm H₂ (Y19405)

X-bar Ti. 500X

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Bright Field

Polarized Light

Fig. 19. RL-4C 13 ppm H₂ (Y19412)

Control

Fig. 20. RL-4C 13 ppm H₂ (Y19413)

Fig. 21. RL-4 23 ppm H₂ (Y19414)

Recombiner

Fig. 22. RL-4 23 ppm H₂ (Y19415)

Fig. 23. CL-2 71 ppm H₂ (Y19416)

Cell

Fig. 24. CL-2 71 ppm H₂ (Y19417)

Zircaloy-2

500X

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Bright Field

Polarized Light

Fig. 25. RL-3C 18 ppm H₂ (Y19406)

Control

Fig. 26. RL-3C 18 ppm H₂ (Y19407)

Fig. 27. RL-3 1600 ppm H₂ (Y19408)

Recombiner

Fig. 28. RL-3 1600 ppm H₂ (Y19409)

Fig. 29. CL-1 37 ppm H₂ (Y19410)

Cell

Fig. 30. CL-1 37 ppm H₂ (Y19411)

X-bar Zr 500X