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IMPROVED ZIRCONIUM ALLOYS

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I. SUMMARY OF PROGRESS TO DATE

To achieve improvement of corrosion properties of zirconium in superheated water and steam, the corrosion behavior of approximately 100 binary alloys was investigated during the first year of work. A complete list of these compositions appeared in Quarterly Report ARF 2198-11, and the results of corrosion studies were summarized in Quarterly Report ARF 2198-18. From the above investigations, fifteen ternary bases were selected for further studies in superheated water or steam; approximately 75 ternary alloys have been arc-melted and fabricated into corrosion specimens. (A complete list of these compositions appeared in Quarterly Report ARF 2198-18).

To date, all specimens for exposure in 680°F water have been placed in test, and data for a two-week corrosion period are available for approximately 35 compositions. At present, preparations are being made for corrosion investigations in 750°F steam, and work is continuing on determining the effect of zirconium purity and heat treatment on corrosion resistance.

II. PRINCIPAL INVESTIGATORS

D. Weinstein	-	Project Engineer
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III. STATEMENT OF PROBLEM

The program objective is the development of zirconium-base alloys having corrosion resistance and/or strength markedly superior to Zircaloy-2 in 680°F water and/or 750° to 900°F steam. The investigation is also concerned with pickup of corrosion hydrogen of experimental alloys, corrosion properties of retained beta structures in Zr-Nb base alloys, and determination of the effect of zirconium purity on corrosion resistance.

IV. DESCRIPTION OF WORK--RESULTS

Corrosion data for the first group of specimens exposed to 680°F water for 336 hours are presented in Table I. Due to the relatively short exposure time, very little can be said of the corrosion properties of these experimental alloys. For this exposure time, all specimens exhibited the desirable tenacious, black oxide coating. Of particular interest is the corrosion behavior of Zr-5Sn-X compositions; the relatively high solubility of tin in alpha-zirconium offers promise for enhanced elevated-temperature strength. Hopefully, the corrosion properties might be equivalent to those of Zircaloy-2.

Work on investigation of the corrosion characteristics of retained-beta alloys has involved preliminary studies of the transformation kinetics of Zr-30Nb, Zr-30Nb-1Mo, and Zr-30Nb-3Mo. Hot rolling these ingots at 1550°F resulted in severe edge cracking and excessive air contamination. Nevertheless, small specimens were beta-quenched from 1000°C and isothermally transformed at 680° and 750°F. The response to heat treatment--that is, transformation of beta--was very poor. Hardness versus transformation time curves did not show the relatively sharp hardness increase which signifies the beginning of beta transformation. The Zr-Nb-Mo alloys have been remelted, and more suitable fabrication techniques will be employed for minimizing edge cracking and contamination.

At present, corrosion specimens are being prepared for investigation of the effect of zirconium purity on corrosion resistance. In the first year of work, specimens of arc-melted sponge, arc-melted crystal bar, and electron-beam melted zirconium all exhibited rapid corrosion in superheated water and steam, and a comparison of properties could not be made. It is well known that the presence of certain alloying elements, such as tin and chromium, counteract the deleterious effect of certain impurities--notably the interstitial gases--on corrosion resistance. Therefore, alloys having the compositions Zr-0.5Nb and Zircaloy-2 were prepared using the three different purity grades of zirconium; by this method, a purity effect--if one exists--ought to be more readily detected.

As shown in Table I, duplicate specimens of a number of compositions are being exposed to superheated water. The reasons for duplication are to obtain very long time corrosion data on selected alloys and to determine hydrogen pickup. While the importance of studying pickup of corrosion hydrogen and its ramifications cannot be overemphasized, the major effort in this program is directed toward improved corrosion resistance. Thus, investigation of hydrogen pickup will be carried out only on compositions exhibiting good corrosion properties in terms of weight gain; of necessity, therefore, these determinations will not be initiated until reasonably long time corrosion data are available. Similarly, the above statements apply to investigation of mechanical properties; tensile strength and other important mechanical parameters will be determined only for those alloys showing good corrosion resistance.

V. FUTURE WORK

The initial two-week test duration for the second group of 680°F water specimens is near completion; the first group has been replaced in an autoclave; after weight gain determination, the second group will re-enter testing. An additional four-week exposure will be allowed before removal of specimens. Specimens for investigation of zirconium purity effects on corrosion resistance will be tested in 680°F water, and work will continue on preparation of corrosion specimens in 750° and 900°F steam. With new ingots of Zr-Nb-Mo, studies will proceed on the corrosion behavior of retained-beta structures.

VI. CONCLUSIONS

This program is concerned with the development of zirconium-base alloys having improved corrosion resistance and/or strength. A major improvement over Zircaloy is desired, and the approach to this development has involved corrosion screening a wide range of binary alloys. These data have pointed out promising alloy bases which have been employed in preparing a large number of ternary compositions. At present, the ternary alloys are being evaluated for corrosion resistance in superheated water and steam; hopefully, a number of these compositions will initially satisfy the program objectives.

VII. REPORTS ISSUED

None

Respectfully submitted,

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TABLE I

INITIAL CORROSION BEHAVIOR OF TERNARY ALLOYS IN 680°F WATER

Composition, w/o	336 Hour Weight Gain, mg/dm^2
Zircaloy-2	18.99
Zr-1Cr-1Sb	17.40
Zr-1Cr-1Sb	14.84
Zr-1Cr-0.5Nb	15.13
Zr-1Cr-0.5Nb	15.81
Zr-1Cr-0.5Sn	16.05
Zr-1Cr-0.25Cu	20.04
Zr-1Cr-0.25Fe	13.47
Zr-1Cr-0.25Fe	12.80
Zr-1Cr-0.25Mo	24.30
Zr-1Cr-0.25Te	16.36
Zr-1Cr-0.25Ge	15.40
Zr-1Sb-0.5Nb	16.36
Zr-1Sb-0.5Nb	15.83
Zr-1Sb-0.5Sn	16.04
Zr-1Sb-0.25Cr	17.14
Zr-1Sb-0.25Cr	17.33
Zr-1Sb-0.25Cu	22.08
Zr-1Sb-0.25Fe	18.97
Zr-1Sb-0.25Fe	19.02
Zr-1Sb-0.25Mo	19.33
Zr-1Sb-0.25Mo	18.37
Zr-1Sb-0.25Te	19.86
Zr-1Sb-0.25Ge	15.37

TABLE I (continued)

Composition, w/o	336 Hour Weight Gain, mg/dm^2
Zr-5Sn-0. 5Nb	18. 24
Zr-5Sn-0. 5Nb	19. 01
Zr-5Sn-1Cr	18. 15
Zr-5Sn-1Sb	18. 98
Zr-5Sn-2. 5Sb	28. 26
Zr-5Sn-0. 25Cr	17. 20
Zr-5Sn-0. 25Cu	21. 31
Zr-5Sn-0. 25Fe	25. 60
Zr-5Sn-0. 25Fe	24. 57
Zr-5Sn-0. 25Mo	21. 93
Zr-5Sn-0. 25Te	19. 05
Zr-5Sn-0. 25Ge	18. 83