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Reading File

-CULM 3922

Pratt & Whitney Aircraft
Connecticut Aircraft Nuclear Engine Laboratory

MASTER

Alkali Metal Corrosion Research

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Introduction

Pratt & Whitney Aircraft, CANEL is currently engaged in the development of a high performance, lithium-cooled reactor experiment under contract with the Atomic Energy Commission. The materials compatibility requirements for the primary coolant system are essentially the same as those for the terminated Aircraft Nuclear Propulsion program with the added requirement for long lifetime. Therefore, the selection of the containment material has been made on the basis of corrosion evaluations and other properties testing performed under the previous program. To validate the selection of materials and extend our knowledge concerning the limits of compatibility, programs are in progress involving (1) long lifetime forced-convection corrosion loop testing, (2) corrosion mechanism studies and (3) chemical analyses of alkali metals. The status of these programs is summarized in this report.

Corrosion Studies

For several years, the corrosion behavior of columbium and its alloys in lithium has been under investigation by PWA-CANEL using forced-convection loops to determine the effect of important engineering parameters. A total of 46,918 hours of forced-convection loop testing with more than 16,263 hours at 2000F and above has shown that Cb-1 Zr alloy is an excellent containment material for high temperature lithium. When environmental conditions during fabrication and testing were controlled to minimize oxygen contamination of the alloy, no evidence of solution or intergranular corrosion effects were observed over the following ranges of conditions:

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Maximum temperature	1800 to 2200F
Thermal gradient	200F and 400F
Lithium velocity	9 to 21 fps
Cooler to heater area ratio	3/1 and 6/1
Heat flux in cooler	5.5 to 52.5×10^4 Btu/hr-ft ²
Test duration	250 to 2000 hours

Limited corrosion tests have been performed as part of a program to determine the maximum temperature for acceptable compatibility between Cb-1 Zr alloy and lithium. Results suggested that the threshold for solution corrosion occurs at approximately 2400F although no evidence of mass transfer deposits was observed in test times up to 500 hours.

A program has been initiated to verify the compatibility of Cb-1 Zr alloy with lithium for long lifetime applications. A forced-convection loop has accumulated more than 4000 hours in a continuing test operating at 2000F and a heat flux of 0.2 to 0.3×10^6 Btu/hr-ft². No evidence of a time-dependent corrosion process is apparent from the loop performance to date.

The compatibility of a lithium-Cb-1 Zr alloy primary coolant circuit combined with a NaK-type 316 stainless steel secondary coolant circuit is being evaluated in a test unit which simulates the bimetallic system and shrouding design of the proposed reactor experiment. The test unit has been run a short time preliminary to a scheduled operation in air at 2000-1600F in the lithium system and 1600 to 1200F in the NaK system.

Much valuable corrosion data are also to be collected from component development tests during the next year. These tests will include full size heat exchangers and centrifugal pumps which are in advanced stages of fabrication from Cb-1 Zr alloy.

In supporting capsule corrosion tests, the correlation between oxygen impurity content in Cb-1 Zr alloy and lithium corrosion was determined quantitatively. Results indicated that the tolerance of Cb-1 Zr alloy for oxygen impurity has been greatly increased as regards corrosion resistance when compared to that of unalloyed columbium. Further tolerance for oxygen is gained by heat treatment of welded material or by increasing the concentration of zirconium or other reactive metal alloying additions. The tolerance of Cb-5 Ti alloy for oxygen impurity is to be determined in future work.

Mechanical relaxation measurements performed on Cb-1 Zr alloy torsion wire specimens provided information on the role of zirconium in improving the lithium corrosion resistance of columbium. Results indicated that the position and movement of oxygen atoms were primarily limited to the vicinity of zirconium atoms when the oxygen concentration did not exceed 0.10 percent. At greater oxygen concentrations, the additional oxygen atoms were located predominantly

in the vicinity of columbium atoms and exhibited an apparent diffusivity similar to that in unalloyed columbium. Thus, the excellent corrosion resistance of Cb-1 Zr alloy at low oxygen levels has been attributed to the immobility of oxygen atoms as a result of the comparatively high binding energy associated with oxygen-zirconium atom interactions. When the interstitial oxygen concentration in the alloy exceeds the quantity which can be associated with zirconium atoms, corrosion typical of unalloyed columbium is to be expected. Future work is to be concerned with oxygen impurity behavior in the columbium-titanium system.

Chemical Analysis Studies

The problem of determining the purity of an alkali metal has been under study from the following aspects: (1) development of methods for determination of impurities, (2) sampling procedures for alkali metals to assure that analytical results are representative of the contents of the system and (3) correlation of results of chemical analyses with those from monitoring devices integral with engineering loops. Methods for the determination of the principle impurities other than oxygen in lithium have been described previously. Recent activities have been aimed at the development of a method for the determination of oxygen in lithium which would be simpler than our modification of the Sax and Steinmetz method. The feasibility of using liquid anhydrous ammonia as a solvent to separate alkali metals from their oxides has been established in experiments principally with lithium. Work is to be continued with the object of completing a statistical validation of the method.

Sampling methods and plugging plate correlation with chemistry are to be studied in a NaK-stainless steel forced convection loop. Oxygen concentrations will be varied by suitable additions of impurities and by change in cold trap temperatures to permit evaluations of the performance of several types of plugging plate, the reliability of sampling devices and the agreement between plugging plate and chemical results.