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NaTHE OXIDATION OF REFRACTORY METALS IN LIQUID SODIUM*

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INTRODUCTION

The purpose of this study was to investigate the oxidation characteristics of various refractory metals for use as getters in sodium coolant purification systems. The molten plutonium fast reactor core concept requires a refractory metal fuel container material (Ta or Ta - W alloy). Cold trapped sodium is not sufficiently pure to maintain a reasonably low oxidation rate of core Ta. Therefore, in order to purify the sodium below cold-trap quality, it is necessary to introduce a large quantity of hot getter material into the system to compete with the core material for the oxygen present. The goal of this investigation is to define the oxidation characteristics of possible hot getters and of the core container material. With this information it should then be possible to predict the kinetics of hot-trapped systems.

OXIDATION IN COLD TRAPPED SODIUM

Experimental Approach

The Hot Trap Evaluation Loop was constructed for the purpose of providing the environmental conditions for this study. The loop has a nominal 1 gpm flow rate with three test sections for sample exposure. A large bypass cold trap is used to control oxygen concentration. Oxygen concentration has been controlled quite well in the range of 10-20 ppm as determined by a plugging indicator and the KAPL solubility curve. Samples are exposed in a temperature gradient of approximately 100°C per 40 in. They are charged and discharged through an inert gas lock system as the sodium loop operates continuously in the temperature range from 500-700°C. The effect of velocity is not being considered as a variable in this experiment. With a nominal 1 gpm flow rate the velocities in the test sections are very low, approximately a 1/10 of a ft/sec..

Materials studied as oxygen getters were Zr, Ta, Ta - 10 W, Nb, 50 Ti-50 Zr and U. Samples were in the form of 1/2 in. square tabs 5 mils thick. Oxidative weight losses were determined based on the assumption Ta and Ta - 10 W oxidize to Ta_2O_5 , Nb oxidizes to Nb_2O_5 , and U oxidizes to UO_2 . 50 Ti-50 Zr alloy

and Zr gained weight. This weight gain is a direct measurement of the oxygen absorbed by the sample. To determine if the weight changes measured were indeed oxygen, samples of Zr and Ta - 10 W were chemically analyzed for oxygen. In the case of Zr which gained weight, the agreement was within experimental error. Ta - 10 W lost weight and the correlation cannot be checked; however, the amount of oxygen gained by the base metal or remaining as a thin film can be determined from the gain in oxygen content. Hardness profiles through the samples were used to determine the depth of oxygen penetration after various exposure times and temperatures.

Discussion of Data

Zr and 50 Ti-50 Zr alloy exhibit weight gain oxidation characteristics. It is believed that the controlling mechanism in the oxidation of these two materials is the combination of adherent film formation and diffusion of oxygen in the oxide and the base metal. For Zr, above approximately 550°C, the data are represented quite well by the correlation:

$$\frac{W}{A} = k(T) \text{ ct}^{\frac{1}{2}}$$

where:

$\frac{W}{A}$ = weight gain per unit area

$k(T)$ = oxidative rate constant (function of temperature only)

c = oxygen concentration in the sodium

t = exposure time.

This is the functional dependence expected for diffusion in a single, finite medium which is, in this case, the base metal. Below 550°C, the weight gain data are spread and suggest the combination of film and base metal diffusion control. A least-squares fit to the data obtained in this study compares favorably with, but is somewhat lower than the weight gain data obtained by other investigators. Many investigators appear to have estimated oxygen concentration based on the

cold trap temperature; this method leaves much to be desired.

Ta - 10 W alloy (and Ta) oxidation data appear to be reasonably well correlated at lower temperatures by the expression:

$$\frac{W}{A} = k(T) ct$$

where:

$\frac{W}{A}$ = oxidative weight loss per unit area

$k(T)$ = rate constant (function of temperature only)

c = oxygen concentration in sodium

t = exposure time

At the temperatures considered and in cold-trap quality sodium, Ta and Ta - 10 W form a very thin non-adherent film which spalls at very early exposure times. At higher temperatures the rate of net weight loss decreases indicating that oxygen has diffused into the base metal in addition to the occurrence of film spallation.

Niobium and uranium data have been accumulated, but no serious attempt to describe the oxidation process has yet been made.

OXIDATION IN HOT TRAPPED SODIUM

Experimental Approach

A hot trap of corrugated Zr foil was fabricated in the form of 5 modules with sample positions between each module. The hot trap was designed to be inserted into the Hot Trap Evaluation Loop through the inert gas lock system. Hot trap modules were weighed prior to and subsequent to the hot trap run. The samples were weighed before and after the run to determine the weight change of various hot trap materials as a function of distance along the flow path through the hot trap. In this way the effect of decreasing oxygen concentration in the sodium, which defies analytical measurement at these levels, was observed in terms of the weight change of the sample materials.

Discussion of Data

Preliminary data consist of that obtained from a single run. A hot trap was run in flowing sodium for 2003 hours at 600°C with a nominal sodium velocity of 0.1 fps. A total area of Zr foil (0.005 in. thick) of $1.08 \times 10^4 \text{ cm}^2$ was exposed. The result was a total weight gain in the hot trap of 1.29 gms. Gettering effectiveness of the sample materials appears to decrease in the following order: 50 Zr-50 Ti, Zr, U, Nb, Ta and Ta - 10 W. It was also observed that the weight change for most materials decreased along the flow path. This indicates qualitatively a concentration profile through the hot trap.

Ta and Ta - 10 W were protected quite well by the Zr hot trap. The effective corrosion rates of Ta and Ta - 10 W were 14×10^{-3} and 3×10^{-3} mils/yr respectively. Ta, Ta - 10 W, Nb, Zr and 50 Zr-50 Ti samples exhibited no visible film during this 2000 hr exposure. However, the Zr in the hot trap had an oxide film which was smoky in appearance. The major difference in the Zr in the hot trap and the Zr in the samples was that the hot trap material was degreased, "as received" Zr sheet; whereas, the samples were vacuum annealed and recrystallized. Uranium also had an oxide film.

HOT TRAP KINETICS

A correlation for the oxidation of Zr has been postulated above. This correlation is based on data obtained in a 10-20 ppm range of oxygen concentration. Since an analytical technique for oxygen in sodium below one ppm is presently nonexistent, the determination of concentration profiles with time in hot trap systems is not possible. However, it is possible to estimate this profile based on data obtained above one ppm.

If one considers a closed loop in which the only oxygen removal mechanism is the hot trap and the only source of oxygen is the initial amount of oxygen in the sodium plus some constant source rate, it is then possible to derive a differential equation which describes the concentration as a function of time:

$$\frac{dc}{dt} = \frac{S - \frac{kAc}{2t}^{\frac{1}{2}}}{(10^{-3}) M + dAt^{\frac{1}{2}}}$$

where:

- M = sodium inventory in the loop - g Na
- c = oxygen concentration at time t - ppm
- t = time - hrs
- S = oxygen source rate - mg O/hr
- A = total area of Zr - cm²
- k = rate constant for a particular temperature - $\frac{\text{mg O}}{\text{cm}^2} / \text{ppm/hr}^{\frac{1}{2}}$.

This equation assumes that the decrease in oxygen concentration per pass through the hot trap is very small and that the source rate is linear with time (and can be determined). If the parameters in this equation are known it is possible to estimate the time-concentration profile in a closed loop. Experimental verification of this method is presently being undertaken.

RESULTS AND CONCLUSIONS

1. The correlations presented provide the ground work for being able to predict hot trap kinetics in a closed loop. The Zr oxidation correlation is best at temperatures above ~550°C. This is in the range of interest for most LASL systems.
2. Oxidation of Ta and Ta - W alloys needs to be better defined. A more complicated mathematical model is needed to correlate the higher temperature oxidation kinetics of this system. This is also true of Zr oxidation for lower temperatures.
3. Although velocity is not believed to be a significant factor in Zr oxidation, oxidation of Ta (and Ta - W alloys) is expected to increase with velocity.

4. 50 Ti-50 Zr alloy appears to be a more efficient hot trap than Zr, but fabrication qualities are not as desirable. The oxidation rates of Ta and Ta - 10 W can be kept below 0.1 mil/yr in Zr hot trapped Na. (This says nothing of oxygen diffusion into the base metal.)