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An Investigation Of

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SCALING OF ZIRCONIUM AT ELEVATED TEMPERATURES

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SCALING OF ZIRCONIUM AT ELEVATED TEMPERATURES

Self Heating Effects

An attempt was made to determine if there was any self-heating effect in the scaling of zirconium specimen in air at 900°C. This was thought to be associated with the breakaway in the scaling curve where the nitride is converted to the oxide with the corresponding exothermic reaction. Thorium specimens show a similar exothermic reaction when scaled in air giving considerable temperature increases to the thermocouples attached to them (1). Thermocouples were attached to several zirconium specimens both on the surface of the specimens and through holes drilled in these specimens. Their positions were chosen such that they would be as close as possible to the reaction interface. In three different runs no temperature rise was observed in any of the couples. This seems to show that if any self-heating effect was present it was not detectable by this method.

Sintering Effects

The white, porous oxide formed on forged zirconium at 900°C in air was stripped from the specimen. This scale when heated in air for 24 hours at 1100°C showed no tendency to sinter.

Role of Hydrogen

Hydrogen analyses were carried out on selected zirconium specimens as follows: (1) Zr as received from machine shop with rough polish - 40 ppm (2) Same as (1) except dipped in 30% H_2SO_4 for 10 seconds and dried in methyl alcohol - 39 ppm (3) Annealed in vacuum, 8 hrs., 600°C, polished - 18 ppm (4) Cleaned in 30% H_2SO_4 , scaled in air for 5 hrs. - 52 ppm (5) Not cleaned in H_2SO_4 , scaled in air at 900° for 5 hrs. 44 ppm

These results indicate that H_2 pickup during pickling in H_2SO_4 is not too significant. In fact the hydrogen difference between any of the above specimens does not appear to be meaningful.

- (1) P. Levesque and D. Cubicciotti, "The Reaction Between Oxygen and Thorium," J. Am. Chem. Soc., 73, 2028 (1951)

In order to isolate hydrogen completely as a factor a zirconium specimen was vacuum annealed at 1.5×10^{-5} mmHg for 24 hours. Pure oxygen (.2N) and nitrogen (.8N) were then admitted immediately. The specimen was relowered into the 800°C zone and scaled giving a breakaway time very close to those of other specimens not annealed but scaled at the same temperature and partial pressures. Thus it seems that only if the specimen is saturated with hydrogen will the breakaway be moved to greater times. (See Quarterly Report No. 11). Below this saturated level there seems to be no effect on the breakaway.

Simulated Scales

Work is now in process to form a scale similar to that which is formed on zirconium when sealed in air by first scaling in air and sandblasting the scale products off to give the saturated metal layer. Next the specimens will be scaled in oxygen, then nitrogen controlling the times to get the desired thicknesses of these scales.

Future Work

The simulated scale specimens will be examined and compared to the regular specimens. They will also be scaled further in various mixtures of oxygen and nitrogen and air and their rates and structures compared with those of other zirconium specimens.

The effect of heating rates will also be examined by holding pure zirconium specimens in air at various positions in the hot zone. The specimens will gradually be lowered to hotter and hotter regions approaching say 800°C. The scaling rates will be noted along with other characteristics of the scale and metal. This should show, when compared with a regular specimen scaled at 800°C in air, whether the more slowly heated specimen will form a scale with less tendency to crack.

Some of the specimens will also be strained after heating in air for various times before the breakaway at 900°C. They will be rescaled and the resultant scaling rates should show the effect of stress on the metal-oxide interface and how it affects the nitride layer. An attempt will also be made to determine the scaling rate while the specimen is under stress.

A few of the 900°C specimens scaled in air will be analyzed for both oxygen and nitrogen content in the metal. This gas content will then be plotted as a function of the scaling time. This would indicate a possible correlation between the gas content and the breakaway time.

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