An Investigation Of
SCALING OF ZIRCONIUM AT ELEVATED TEMPERATURES

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SCALING OF ZIRCONIUM

Current Work

During the last quarter, work was continued on a study of the effect of various diffusion zones (gas penetration) on the scaling behavior of iodide zirconium in air. Specimens 0.06" thick were prepared by first pretreating samples at 800° or 900°C in the following atmospheres: air, 30 oxygen-70 nitrogen, oxygen, nitrogen, and hydrogen. The scales formed in the various atmospheres were removed by sandblasting, or, as in the case with the nitrogen atmosphere, the nitride scale was removed on metallographic polishing papers, thus exposing the saturated metal layer. No scale was formed in the hydrogen atmosphere. After removal of the scale layers the specimens were immersed in a dilute sulfuric acid solution, and rinsed and dried with alcohol before scaling in air at 900°C.

The course of the reaction in air was followed by calculating the instantaneous scaling rate, F , at various times.

$$F^* = \frac{\frac{A}{A_o} \cdot \frac{d\left(\frac{W}{A_o}\right)}{dt} - \frac{W}{A_o} \cdot \frac{d\left(\frac{A}{A_o}\right)}{dt}}{\left(\frac{A}{A_o}\right)^2}$$

where,

W = weight increase of the specimen, mg.

A_o = original surface area, cm²

A = instantaneous surface area, cm²

t = scaling time, hours

* See First Technical Progress report, March 1955.

This method of studying the kinetics of the reaction was employed since it gives a truer representation of the scaling behavior since, in many cases with zirconium, the metal is deforming such that the surface area is increasing during the scaling runs. The instantaneous scaling rates for the runs in air after removing the scale formed in a prescaling atmosphere are shown in Figs. 1-6.*

Air-Air Combination

Scaling runs in air after removing prescales formed in air, Fig. 1, show that the scaling rate is raised and the breakaway time is shortened as compared to the initial run in air; otherwise, the curves are similar in shape. An interesting feature here is that magnitude of the scaling rate and time at which breakaway occurs are relatively independent of prescaling times exceeding one hour. This is not too surprising since it was shown in earlier studies (See Quarterly Report No. 14, December 1956) that the depth of the diffusion zone in specimens scaled in air is constant beyond a scaling time of about one hour.

The above runs were carried out with regular-size specimens (0.06" thick before prescaling). With oversize specimens (0.246" thick) the deleterious effect of the initial presence of a diffusion zone was also noted, Fig. 2; however, the shape of the curve was not

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It will be recalled that similar plots were presented earlier (see Third Technical Progress Report, December 1956; and Quarterly Report No. 15, March 6, 1957) for a study of the effect of different prescales (not removed) on the scaling behavior in various atmospheres.

the same as that obtained with a regular-size sample. The greater depth of the diffusion zone in oversize specimens may be responsible for this behavior.

Mixture of Pure Gases (O_2 - N_2)-Air Combination

The scaling behavior in air of a specimen with a diffusion zone formed in a 30% O_2 -70% N_2 mixture is identical with a comparable run using air as the prescaling medium (cf. Figs. 2 and 3).

Oxygen-Air Combaintion

Scaling runs in air after forming a diffusion zone in oxygen, Fig., reveal that the breakaway is accelerated and the initial scaling rate is progressively increased as the prescaling time is lengthened. For long prescaling times, the breakaway in the curve disappears. The latter finding may be associated with the fact that the depth of the diffusion zone continually increases with increasing prescaling time in oxygen, as contrasted to the constant depth of diffusion zone obtained when prescaling in air beyond one hour.

Nitrogen-Air Combination

In exposing specimens with a nitrogen-saturated diffusion zone to air, both the initial scaling rate and time for breakaway increased as the prescaling time in nitrogen was increased, Fig. 5. As with oxygen prescaling, the depth of the diffusion zone in specimens prescaled in nitrogen is greater for longer prescaling times.

Hydrogen-Air Combination

Pretreatment in hydrogen greatly increases the breakaway time upon subsequent scaling in air, but does not alter the initial scaling rate, Fig. 6. In all probability, hydrogen complicates the scaling behavior in air by diffusing outward and acting as a protective cover toward metal oxidation.

Future Work

Preliminary results indicate that hafnium as a major impurity in zirconium influences the scaling behavior. An effort to produce quantitative data on the effect of hafnium will be made.

FIG 1: INSTANTANEOUS SCALING RATE IN AIR AT 900°C AFTER REMOVING PRESCALE FORMED IN AIR AT 900°C FOR THE INDICATED TIMES.

FIG. 2: INSTANTANEOUS SCALING RATE OF OVERSIZE SPECIMEN - (0.246" THICK) AFTER REMOVING PRESCALE FORMED IN AIR AT 900°C FOR THE INDICATED TIME.

FIG. 3 : INSTANTANEOUS SCALING RATE IN AIR AT 900°C AFTER REMOVING PRESCALE FORMED IN 30% OXYGEN-70% NITROGEN MIXTURE FOR THE INDICATED TIME.

FIG. 4: INSTANTANEOUS SCALING RATE IN AIR AT 900°C AFTER REMOVING PRESCALE FORMED IN OXYGEN AT 900°C FOR THE INDICATED TIMES.

FIG. 5: INSTANTANEOUS SCALING RATE IN AIR AT 900°C AFTER REMOVING PRESCALE FORMED IN NITROGEN AT 900°C FOR THE INDICATED TIMES.

FIG. 6: INSTANTANEOUS SCALING RATE IN AIR AT 900°C AFTER PRESCALING IN HYDROGEN AT 800°C FOR THE INDICATED TIME.