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Studies in Zirconium Oxidation

This study was undertaken to provide insight into the oxidation mechanism of zirconium by combining electrical measurements with oxidation data. The measurement of electrical potential across growing scale on zirconium and the determination of conventional weight-change oxidation data were carried out at 550°, 700°, and 800°C.

A report has been prepared which covers investigations of several independent topics. Oxidation rate is determined by standard methods to provide a base against which to compare the electrical measurements. The rate-limiting process and phase transformation are also studied, assessing the effect of volume change associated with tetragonal-monoclinic transformation as one of the causes for crack formation in the oxide.

The potential across the growing oxide is investigated as a function of the influence of oxygen partial pressure at moderate-to-low pressures, and compared against weight-loss data under the same partial pressure conditions. Measurements were also made under conditions involving zirconium reactions with nitrogen, carbon dioxide, and water vapor.

The following is a brief summary of some of the results: Zirconium oxidation at 550°, 700°, and 800°C follows rate lines that are between parabolic and cubic on a log-log plot, but not on a straight line. The oxidation kinetics are practically independent of the partial pressure of oxygen in pressures between 1 and 400 mm.

Resistance measurements of the oxide film at different stages of oxidation suggest predominantly

electronic control of oxidation, though control during the initial stages of oxidation was significantly ionic. This change is interpreted as being caused by the transformation of the initially formed tetragonal zirconia to the monoclinic modification.

No measurable potential was produced in high-temperature nitriding of zirconium, although even small amounts of oxygen added to a Zr+N₂ system react to yield the oxide.

Carbon dioxide oxidation of zirconium apparently involves a different mechanism and surface process. Resistance measurements and results of admission of a small amount of oxygen indicate that a different oxidation product probably is formed during CO₂ oxidation.

Notes:

1. Additional information and data are contained in *Studies in Zirconium Oxidation*, by J. Levitan, J. Draley, and C. Van Drunen, ANL-7252, December 1966, Argonne National Laboratory, Argonne, Illinois. This report is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151; price: \$3.00; microfiche \$0.65. Two other references to related work are: (a) D. H. Bradhurst, J. E. Draley, and C. J. Van Drunen, "An Electrochemical Model for the Oxidation of Zirconium," *Journal of the Electrochemical Society*, 112, p. 1171-1177 (1965). (b) J. Levitan, J. E. Draley, and C. J. Van Drunen, "Low-Pressure Oxidation of Zirconium," *Journal of the Electrochemical Society*, 114, p. 1086-1089 (1967).

(continued overleaf)

2. Inquiries concerning this innovation may be directed to:

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Patent status:

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