

KINETICS OF CLADDING OXIDATION IN AN AIR ENVIRONMENT

Background

The kinetics of fuel rod cladding oxidation in an air environment is an important consideration in many safety-related investigations. In spent fuel pool accidents arising from a loss of water inventory, fuel rods can be exposed to an air environment. Structural failures of spent fuel dry casks during storage and transportation may also provide pathways for air intrusion and consequent oxidation of spent fuel rods.

Knowledge of air oxidation kinetics at relatively low temperatures [300–600 EC (572–1,112 EF)] is helpful to determine the margin for cladding integrity in the above instances. Prior data on cladding oxidation in air environments were based on experiments at higher temperatures [\$800 EC (1,472 EF)], and the results were analytically extrapolated for application to the low-temperature range of interest. The U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Regulatory Research (RES), initiated an experimental research program at the Argonne National Laboratory (ANL) in July 2002 to obtain experimental data on the air oxidation kinetics of Zircaloy-4, Zirlo, and M5 claddings, which are representative of the current and/or projected cladding inventory in operating reactors and in spent fuel that is discharged after medium or high level of fuel burnup. The program was completed recently, and the NRC subsequently published NUREG/CR-6846 and NUREG/CR-6851 (References 1 and 2, respectively) to document the results, which provide a more realistic analysis of fuel and cladding heatup in an air environment.

Overview of the Program

The experimental research conducted by ANL comprised a series of experiments, in which unirradiated specimens of Zircaloy-4, Zirlo, and M5 cladding were subjected to isothermal air oxidation at different temperatures and for different durations. The cladding materials selected for this study are all zirconium-based alloys with small amount of impurities and secondary phase particles. Zircaloy-4 is the most widely used fuel cladding for pressurized-water reactors, particularly for medium burnup operation, and constitutes much of the older inventory in spent fuel pools. Zirlo and M5 claddings are designed for high burnup operation and reportedly exhibit lower corrosion rates (i.e., lower oxide layer growth) than Zircaloy-4 during in-reactor operation.

One series of experiments conducted by ANL investigated the effect of a pre-existing oxide layer, as expected at end-of-life reactor conditions, on further oxide layer growth during air oxidation of cladding. The pre-existing layer simulated steam oxidation of cladding during in-reactor operation and, in that sense, unirradiated samples were prototypic of irradiated cladding. Another series of experiments investigated air oxidation kinetics of bare cladding to provide a data set for comparison with the tests in the previous series. A third series investigated the kinetics of air oxidation in a nitrogen-rich environment to simulate the effect of nitriding on cladding in a situation where the air is largely depleted of oxygen. The final series of experiments investigated the effect of pre-existing hydrides, which form on cladding surfaces during in-reactor operation and are particularly relevant for high burnup operation. Such hydrides are believed to have potential deleterious effects on subsequent oxidation kinetics and the mechanical behavior of cladding. As a bounding case, ANL used pre-hydrated Zirlo specimens in the final series of experiments.

Results

The results of the air oxidation kinetics study are discussed in detail in NUREG/CR-6846 and NUREG/CR-6851 (References 1 and 2, respectively). The experimental data provide three sets of measurements, including weight gain of the cladding as a result of air oxidation, increased oxide layer thickness as measured by scanning electron microscopy (SEM), and oxygen and hydrogen pickup as measured by chemical analysis. These measurements are complimentary to each other. The results are conventionally described as a function of exposure time.

The weight gain and the oxide layer thickness data were used to develop correlations that relate oxidation rate and temperature using an Arrhenius-type equation, as follows:

$$\text{Rate constant} = A \exp(-B/T)$$

where A and B are empirical constants, and T is the isothermal oxidation temperature. The oxidation rate constants for steam pre-oxidized Zircaloy-4, Zirlo, and M5 are plotted in Figure 1 in terms of the oxide layer growth, and in Figure 2 in terms of the weight gain data. Figure 2 also shows the extrapolated data based on the "NUREG1" and "NUREG2" correlations, which were derived from the high-temperature studies discussed in References 3 and 4, respectively.

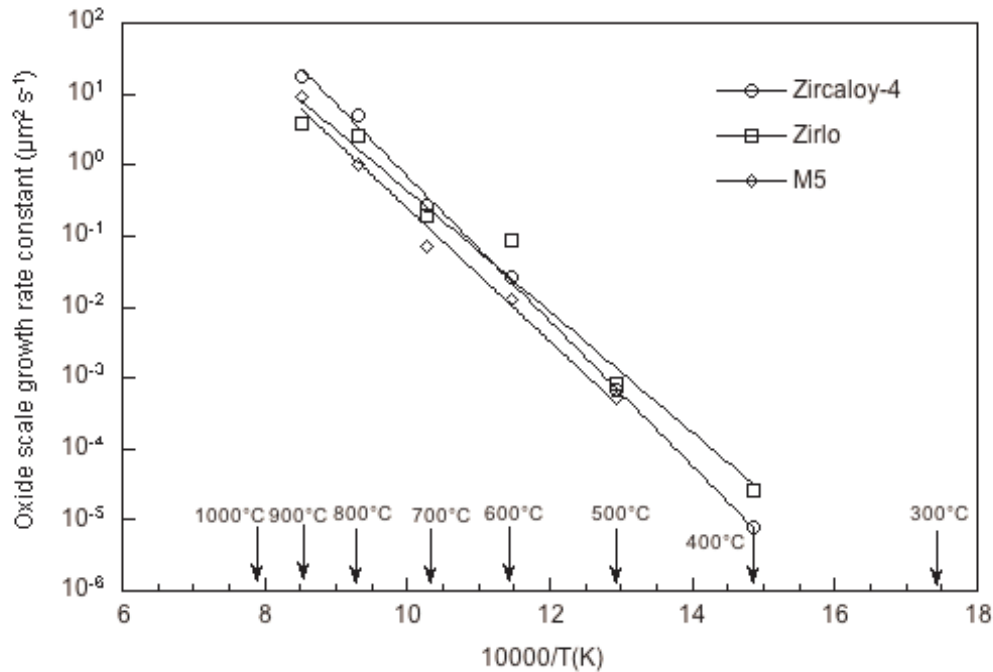


Figure 1. Oxide growth rate constants for steam pre-oxidized Zircaloy-4, Zirlo, and M5

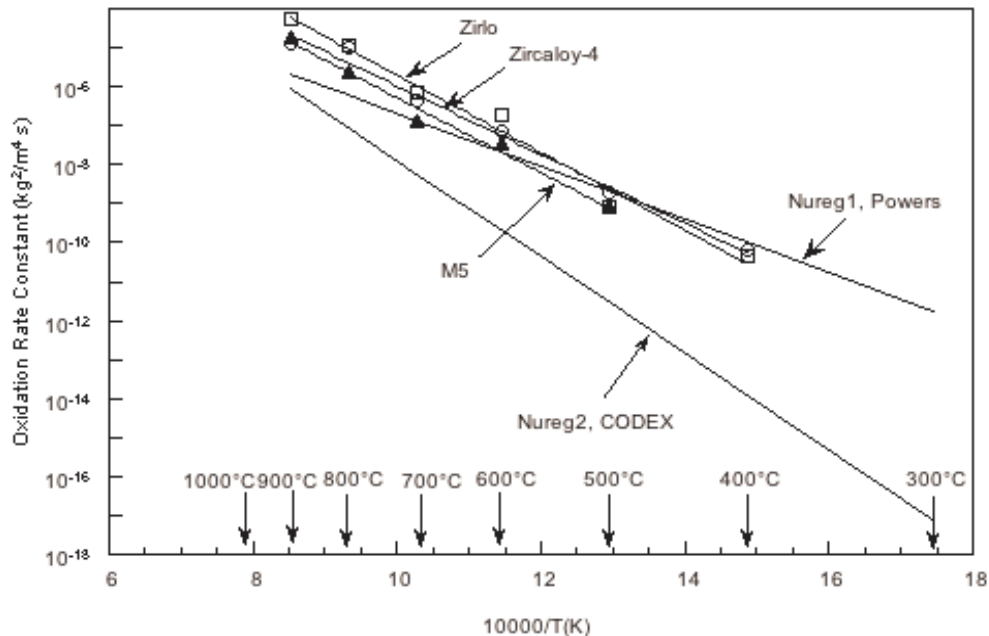


Figure 2. Comparison of air oxidation rate constants of Zircaloy-4, Zirlo, and M5.

A comparison of the oxidation rate constant data for the various cladding types reveals that Zirlo and Zircaloy-4 have similar air oxidation kinetics, with slightly faster oxide growth in Zirlo at temperatures lower than 600 EC (1,112 EF). By contrast, the air oxidation kinetics of M5 are bounded by those of Zirlo and Zircaloy-4. The air oxidation rate of the bare cladding (i.e., not steam pre-oxidized) is generally comparable to or slightly higher than that of the pre-oxidized cladding for the temperature range of interest. This suggests that a pre-existing oxide layer may slow down further oxidation. Also, the oxidation of cladding in a nitrogen-rich environment is comparable to that in air, which suggests that nitriding has little, if any, effect on oxidation kinetics.

Clearly, the oxidation rates of all three cladding types are bounded by those in References 3 and 4 (denoted in Figure 2 as NUREG1 and NUREG2, respectively). More appropriately, the experimentally derived oxidation rates agree closely with those in Reference 3. The latter correlations were derived analytically on the basis of experimental data at and above 1,000 EC (1,832 EF) and extrapolated to lower temperatures. The correlations in Reference 4, which give much lower oxidation rates, were derived from CODEX experiments performed under the European Commission's Fourth Framework Program.

In addition, the oxide thicknesses observed upon air oxidation of pre-hydrated Zirlo specimens were similar to those observed during air oxidation of bare Zirlo specimens. However, comparing the air oxidation data for pre-oxidized specimens only to the data for pre-hydrated plus pre-oxidized specimens indicates that pre-hydrating followed by steam pre-oxidation has more of a retarding effect on further air oxidation at the temperature range considered in this study. With regard to the potential effect on the mechanical behavior of cladding, we note that steam pre-oxidation has a softening effect that is more significant than the hardening effect attributable to pre-hydrating.

Regulatory and Safety Implications

The research results reported herein provide best estimate correlations for air oxidation kinetics of Zirconium-based alloys in the range of 300–900 EC (572–1,652 EF). These correlations can be used in calculating cladding heatup in air and steam/air environments under accident conditions resulting from a loss of coolant inventory in spent fuel pools or dry cask storage.

The experimental results indicate that a pre-existing oxide layer from in-reactor operation does not have any discernible deleterious effect on further cladding oxidation in air environments. In addition, the results confirm that the correlations developed in this study agree well with those that the NRC previously used for the risk analysis of spent fuel pools (Reference 5).

Similarly, the experimental results show that pre-existing hydrides do not have a noticeable deleterious effect on air oxidation of Zirlo cladding that has previously been oxidized in a steam environment during in-reactor operation. Compared to Zirlo, M5 cladding is known to pick up less hydrogen during in-reactor operation and, hence, the effect of hydrides may be even less significant for M5. By contrast, Zircaloy-4 is known to pick up more hydrogen than either Zirlo or M5. However, the fuel rods with Zircaloy-4 cladding in the spent fuel pool inventory are generally older and have much less decay heat than those clad with Zirlo or M5. As such, the Zircaloy-4 cladding is not prone to accelerated oxidation kinetics, especially those discharged at medium burnup.

References

1. NUREG/CR-6846, "Air Oxidation Kinetics for Zr-Based Alloys," prepared by Argonne National Laboratory, U.S. Nuclear Regulatory Commission, Washington, DC, July 2004.
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3. NUREG/CR-6218, "A Review of the Technical Issues of Air Ingression During Severe Reactor Accidents," prepared by Sandia National Laboratories, U.S. Nuclear Regulatory Commission, Washington, DC, September 1994.
4. INV-OPSA(99)-P008, "Oxidation Phenomena in Severe Accidents," Final Report, European Commission Joint Research Center, Ispra, 2000.
5. NUREG-1738, "Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants," U.S. Nuclear Regulatory Commission, Washington, DC, February 2001.