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Short communication

Sensitivity of measured steam oxidation kinetics to atmospheric control and impurities

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ABSTRACT

The most direct means of improving the ability of water cooled reactors to withstand excessive cladding oxidation during a loss of coolant accident is to either modify or replace zirconium cladding. It is important to understand what level of agreement is to be expected as a function of systematic differences in steam oxidation testing techniques and instrumentation among testing facilities. The present study was designed to assess the sensitivities of some of the current and proposed reactor cladding materials. Steam oxidation sensitivity of Zircaloy-2, FeCrAl and Mo to O_2 impurities in steam were examined. It was shown that the effect of O_2 impurities is negligible for the two former materials while significant in the case of Mo.

1. Introduction

Excessive cladding oxidation is the most prominent failure mode for a light water reactor (LWR) nuclear fuel during an extended loss of cooling accident scenario [1]. The most direct means of improving the ability of water cooled reactors to withstand such an occurrence is to either modify or replace zirconium cladding with a material that exhibits improved steam oxidation resistance at elevated temperatures. It is generally accepted that a candidate cladding material must display oxidation resistance to steam at temperatures in excess of 1200 °C for it to be considered accident tolerant with respect to steam oxidation [1].

A number of worldwide research programs are currently evaluating material systems with this objective. Proposed cladding options extend from Fe-based alloys optimized for oxidation resistance and performance under LWR irradiation conditions to revolutionary composites that incorporate functionally graded coatings to mitigate oxidation at high temperature.

The oxidation resistance of a candidate cladding material is one of many metrics that a material must satisfy to be considered for commercial deployment, though it is one of the more readily tested given the focus on accident tolerant fuel cladding development. National laboratories, universities, and industrial partners all contribute to the broad base of data on the oxidation tolerance of various candidate cladding materials, each employing non-standardized experimental equipment and testing procedures. It is important to understand what level of agreement is to be expected as a function of these systematic differences to both facilitate academic dialog and assess observed discrepancies.

Recent screening tests performed to evaluate molybdenum as a possible LWR cladding material provide an extreme example of such discrepancies. Nelson et al. concluded that, while Mo will oxidize rapidly in air at high temperatures, the oxidation rate is muted significantly in water vapor [2]. However, Pint et al. observed nearly three orders of magnitude higher oxidation under reportedly similar conditions [3]. Identification of the source of this difference in observed performance is essential to assessing the feasibility of Mo-based LWR cladding concepts. Further, the cause of such a substantial variance in what is conventionally believed to be a straightforward testing technique may have far reaching implications to the development, deployment, and ultimate success of certain accident tolerant cladding concepts.

In academic reporting, typically only the percentage of steam used is reported, for example 10% water vapor in either air or Ar is a common test parameter for steam turbine applications. If air ingress is excluded [4] evaluation of cladding materials for LWR service with an emphasis on accident behavior instead requires focus on water alone as the oxidizing species. Therefore, research in this area tends to focus on testing under 100% steam atmospheres.

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However, the means used by researchers to obtain and verify the purity of steam used to perform cladding oxidation studies is largely unreported in academic literature. The absence of applicable steam oxidation standards further complicates comparison of oxidation measured among laboratories.

The present study was designed to assess the sensitivities of current and advanced reactor cladding materials to O_2 impurities in steam introduced by testing protocols or instrumentation. The aim of the work is not to provide minimum performance criteria for test instrumentation, but rather to motivate more detailed reporting of experimental parameters, (i.e. including flow rates, purge/carrier gases, system evacuation procedures, etc), since these can have an effect on the residual O_2 in the system.

2. Steam oxidation testing

There are several experimental variables to be considered when steam oxidation testing. The authors will briefly outline a number of these variables, but the bulk of these are not the focus of the experimental work presented; though the effects of these variables are worth consideration by a researcher when planning and reporting on steam oxidation. Many are limited by the instrumentation available to a researcher.

2.1. Dynamic vs static testing

There are two ways to monitor steam oxidation rates during testing: dynamic and static. In a dynamic oxidation test, either the sample's weight change is monitored in-situ via thermogravimetric analysis (TGA) [5] or the amount of hydrogen off-gas, the byproduct of the steam oxidation reaction, is measured using a variety of methods such as utilization of a eudiometer [6,7] or a calibrated mass spectrometer at the exhaust [4,7,8]. In a static test, the sample weight is measured at the beginning and end of an oxidation test. Multiple oxidation tests are required to study oxidation dynamics via static testing. However, these two methods should produce comparable results for the same material and atmospheric conditions. Static oxidation testing is widely used due to its ease of set-up and sample accommodation, and although data collection is more cumbersome, enhanced flow uniformity and relaxed limits on specimen geometry are possible.

2.2. Sample configuration

Sample configuration is likely the second most widely varied experimental condition. Static testing systems can accommodate multiple samples in a single test. Samples can be either hung vertically or aligned horizontally in a tube furnace while steam is purged through the tube. The nature of dynamic testing in a TGA requires one sample is tested at a time. Sample placement on either a flat surface of hanging fixture introduces yet another important variable: the flow velocity of steam across the sample surface. Inherently a hanging sample will experience a more laminar flow pattern. Of course sample materials can vary depending on lot and supplier, necessitating independent elemental analysis to truly compare one study to the next.

2.3. Steam purity

Other variables which can introduce inconsistencies in reported data from one test system to another include furnace fixturing, thermocouple type, placement and calibration, gas flow velocities, thermal profiles (ramp vs isothermal oxidation testing), and gas purity.

The effect of steam purity will be the focus of this correspondence, as it can lead to orders of magnitude discrepancies in measured oxidation when available O_2 is the oxidation rate limiting factor. Several of the candidate claddings currently under investigation are variants of materials which have well understood behavior in steam and O_2 environments, e.g. Cr- and Al-containing steels. As lesser-understood families of materials are explored, little experience exists concerning their steam oxidation behavior and therefore more attention must be paid to the experimental testing parameters which could affect the measured oxidation.

2.3.1. Sources of oxygen impurities in steam

For materials which do not form passivating oxide layers, O_2 control becomes paramount to accurate steam oxidation reporting, particularly at $T < 1000\ ^\circ C$. Oxygen impurities can originate from a number of sources.

2.3.1.1. Air ingress. Air ingress during sample loading can be minimized using vacuum cycles prior to testing provided the system is equipped with a vacuum pump. The ability to evacuate a system prior to testing is necessary to efficiently minimize O_2 contamination. In addition, furnaces with open exhaust ports to air near the sample can lead to additional air ingress during testing. In addition to air ingress during sample introduction and back-flow of air through exhaust ports, atmospheric oxygen leaks in gas fittings and equipment mating seals are a challenge inherent to any process where purge/carrier gas purity is of extreme importance.

2.3.1.2. Carrier and purge gases. Most steam oxidation testing systems employ carrier and purge gases to provide for efficient steam flow through the system. Using an air cover gas will inherently increase the O_2 in the system. Even commercially purchased gases can contain meaningful levels of oxygen impurities. For example, commercially purchased 'Ultra High Purity' (UHP) Ar is often measured to have up to 15 parts per million (ppm) O_2. For samples with strong oxygen affinities, such as zirconium, molybdenum, and tungsten, this can cause oxidation in an atmosphere otherwise believed to be inert.

2.3.1.3. Partial pressure of O_2 in high temperature steam. In addition to system leaks and purge gas impurities, steam dissociates at elevated temperatures to produce a temperature dependent

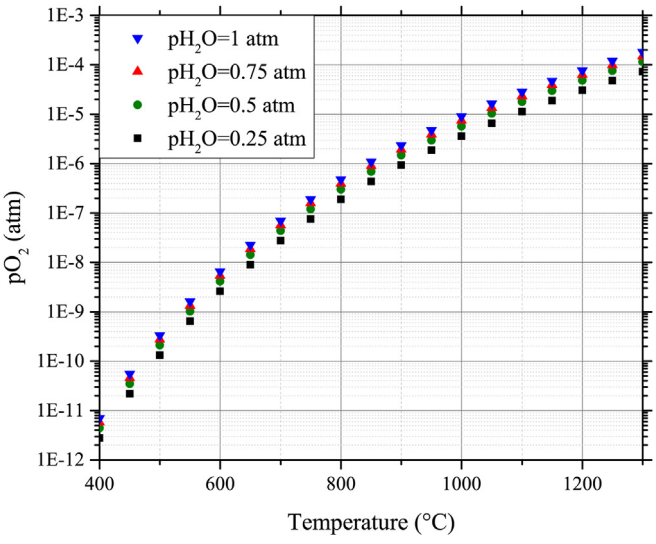

Fig. 1. Plot of the partial pressure of O_2 in 0.25, 0.5, 0.75, and 1.0 atm H_2O as calculated using the Law of Mass Action.