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Severe Accident Test Station (SATS) Activity Report

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Severe Accident Test Station (SATS) Activity Report

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Introduction

Enhancing safety margins in light water reactor (LWR) severe accidents is currently the focus of a number of international R&D programs. The current UO_2/Zr-based alloy fuel system is particularly susceptible since the Zr-based cladding experiences rapid oxidation kinetics in steam at elevated temperatures. Therefore, alternative cladding materials that offer slower oxidation kinetics and a smaller enthalpy of oxidation can significantly reduce the rate of heat and hydrogen generation in the core during a coolant-limited severe accident [1-2]. In the U.S. program, the high temperature steam oxidation performance of accident tolerant fuel (ATF) cladding solutions has been evaluated in the Severe Accident Test Station (SATS) at Oak Ridge National Laboratory (ORNL) since 2012 [3-5]. This report summarizes the capabilities of the SATS and provides an overview of the oxidation kinetics of several candidate cladding materials. A suggested baseline for evaluating ATF candidates is a two order of magnitude reduction in the steam oxidation resistance above 1000ºC compared to Zr-based alloys. The ATF candidates are categorized based on the protective external oxide or scale that forms during exposure to steam at high temperature: chromia, alumina, and silica. Comparisons are made to literature and SATS data for Zr-based alloys and other less-protective materials.

Severe Accident Test Station at ORNL

The SATS is a modular facility located at ORNL. It consists of four separate yet complementary modules meant to provide the ability to comprehensively examine oxidation kinetics and accident response of cladding materials. Figure 1 provides a schematic of the modules. The first module is a thermogravimetric analysis (TGA) unit that offers continuous mass change data for a specimen exposed to 1 bar steam (Rubotherm model DynTHERM LP-HT-II). The second module is the high temperature furnace that is capable of exposing samples to 1 bar steam at up to 1700°C with faster flow rates. The third module is the high-pressure or "Keiser" (named after its builder) rig that enables steam exposures up to 30 bar. The last module is the integral LOCA test furnace that enables rapid ramp rates owing to its infrared furnace technology and is capable of burst testing and quenching of tube specimens. Table 1 provides a summary of operating parameters for these various modules.

Steam is generated in the various SATS modules using deionized water with a nominal oxygen content of ~8 ppm. More extensive oxygen control (such as deaerating by Ar or N_2 bubbling) is not utilized because the majority of testing is conducted at 1200°C and higher. Figure 2 shows that the equilibrium partial pressure of oxygen in pure H_2O at 1200°C is calculated to be 71 ppm and the value rises by an order of magnitude at 1500°C. However, at lower temperatures the equilibrium values are much lower, below 1ppm at ~800°C.

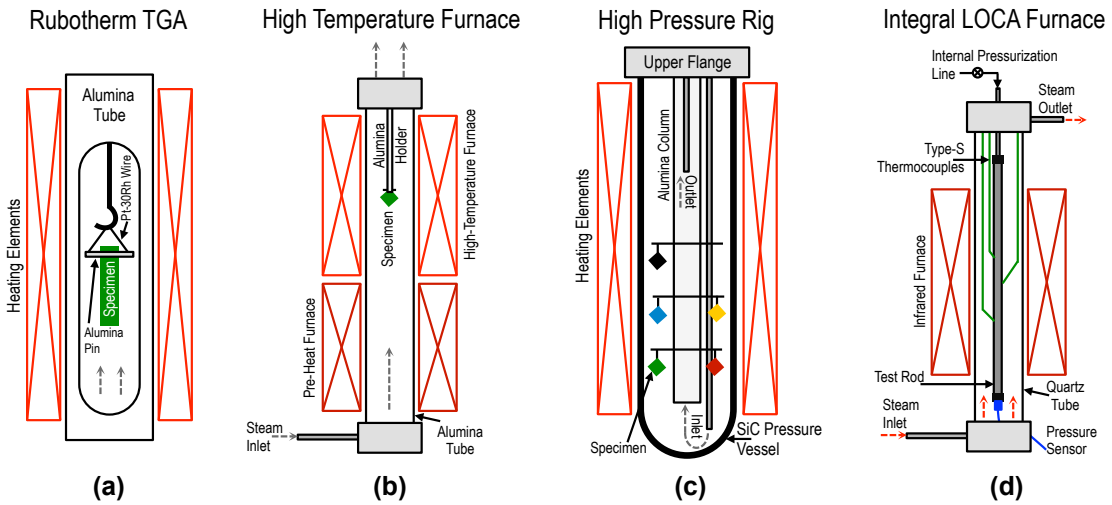

Figure 1. Schematic drawing of the SATS modules.

Table 1. Operating parameters for the various modules of SATS.

	Integral LOCA Furnace	High Temperature Furnace	High Pressure Furnace	Thermogravimetry
Max Temperature [°C]	1200	1700	1400	1550
Max Pressure [MPa]	0.1	0.1	2	0.1
Max Flow Velocity [cm/s]	50	200	2	5
Max Ramp Rate [°C/min]	300	20	20	20
Capable of 100% steam	x	x	x	x

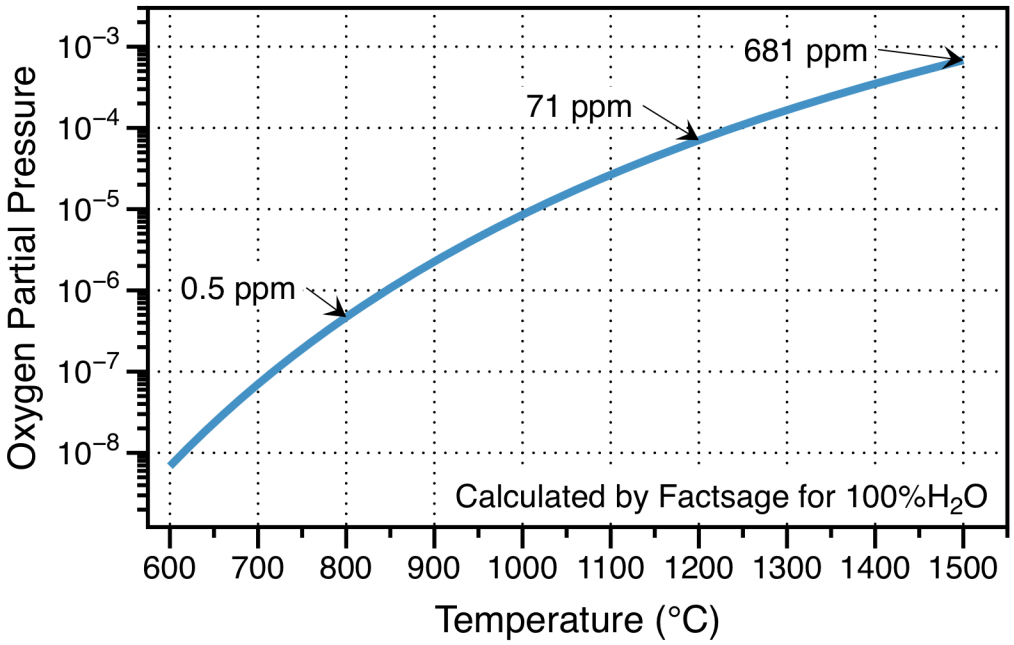

Figure 2. Calculated equilibrium oxygen partial pressure in pure steam as a function of temperature.

Steam Oxidation Kinetics for Candidate Cladding Materials

1. Chromia-forming alloys.

Thermally grown scales rich in Cr are the least stable and fastest growing protective scales but also the most technologically relevant since they form on ferritic Fe-Cr alloys and austenitic Fe-Cr-Ni (stainless steels) and Ni-Cr alloys. For Fe-base alloys there is a large difference between those alloys that are able to form a protective Cr_2O_3 layer and those that rapidly form FeO_x, as indicated in Figure 3. Type 304 stainless steel (SS) with ~18Cr/8Ni is unable to form a protective scale in steam. In contrast, type 310 SS (25Cr/20Ni) forms a Cr_2O_3 scale, as does commercial ferritic E-Brite steel (26Cr-1Mo). Type 446 SS (24.5%Cr) formed a protective scale at 1000°C but showed accelerated oxidation at 1200°C, Figure 3, with the rate near the end of the 4h test being similar to type 304 SS. Thus, chromia-forming Fe-base alloys essentially meet the 100X slower growth rate goal (noted in Figure 3), while steels that cannot form chromia do not meet the goal. (Note: E-Brite and 446 SS are currently being investigated under the General Electric FOA work at ORNL.)

These observations are consistent with early results conducted in Ar-50%H_2O on model Fe-Cr alloys with additions of Mn, Si and Y to enhance their oxidation resistance [6]. Only the alloys with 22.5 and 25%Cr were able to form a protective chromia scale at 1200°C for 24h. The other alloys showed high mass gains indicating the formation of FeO_x oxide nodules. However, the high Ni contents of type 310 SS make that alloy unattractive from a neutronics standpoint and the high Cr contents required in ferritic alloys like E-Brite are prone to embrittlement due to α′ formation under irradiation [1-2].

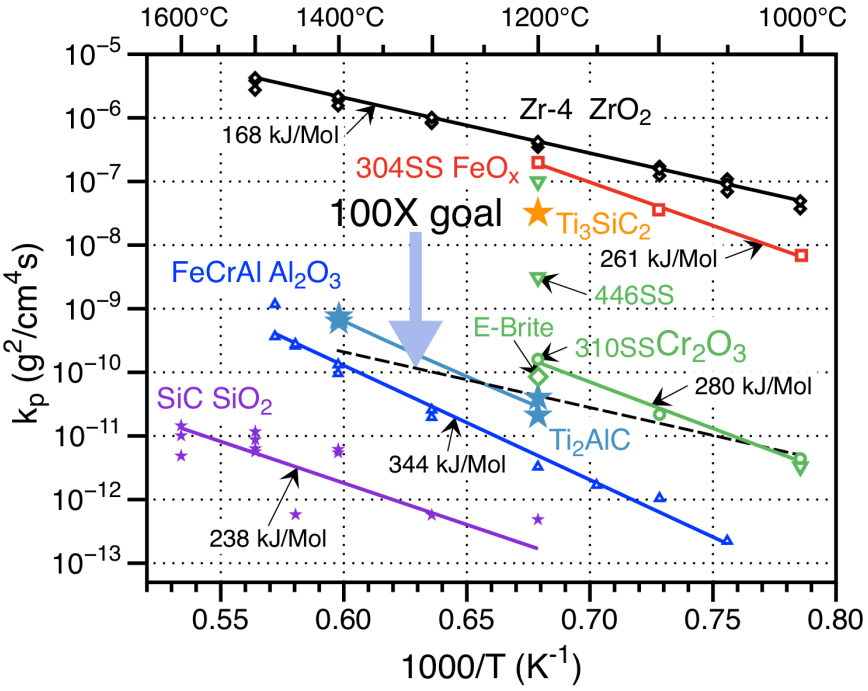

Figure 3. Arrhenius plot of the steam oxidation rate constants and activation energies for various candidate materials. Literature values for Zircaloy-4 are shown for reference.

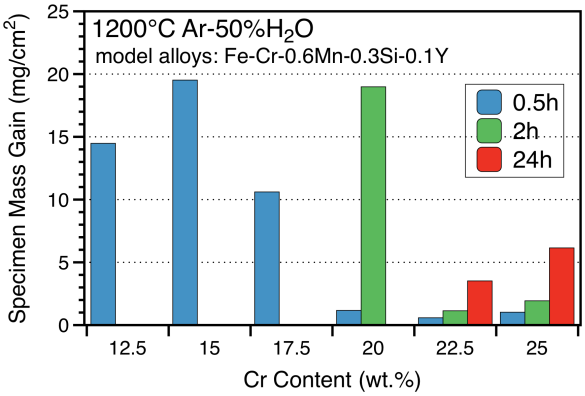

Figure 4. Specimen mass gains in Ar-50%H_2O at 1200°C for model Fe-Cr-0.6Mn-0.3Si-0.1Y alloys as a function of their nominal Cr content. Only the alloys with 22.5 and 25wt.%Cr were able to form a protective Cr-rich scale for 24 h.

2. Alumina-forming materials.

Figure 1 shows two different alumina-forming materials. A higher rate constant was observed for Ti_2AlC MAX phase materials compared to FeCrAlY alloys like Kanthal alloy APMT. This difference was attributed to the formation of some Ti-rich oxide on Ti_2AlC in the presence of steam and dependent on the purity (i.e. presence of TiC) of the MAX phase [7]. While APMT and conventional Fe-20Cr-5Al+Y wrought materials have excellent steam oxidation resistance up to 1475°C, the high Cr content is a concern, as mentioned above for Fe-Cr alloys. Thus considerable effort has been made to identify the critical Al and Cr contents needed to form alumina in steam. The steam oxidation results of numerous commercial and model alloys at 1200°C are summarized in Figure 5. While there is not a definitive composition line that can be drawn, it is clear that below 15%Cr only Al contents above 4% are protective.

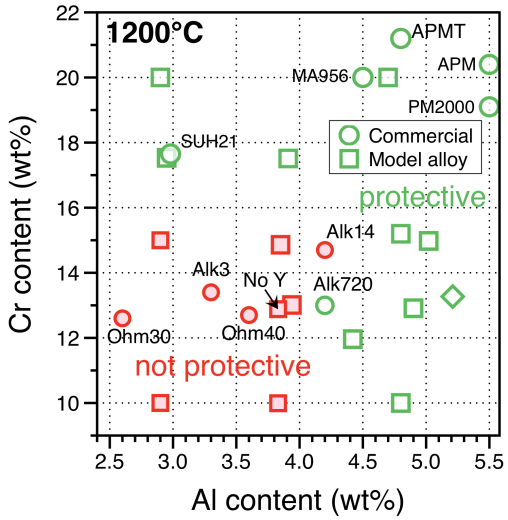

Figure 5. Effect of Cr and Al alloy content on steam oxidation resistance at 1200°C in commercial (circles) and model (squares) FeCrAl alloys. Compositions that form a thin, protective alumina scale are shown with open symbols (green) and those that cannot form alumina in steam with shaded symbols (red).

A second phase of composition evaluation is now in progress as indicated in Figure 6. The results from the first alloy test matrix are shown in Figure 5 and the second series of alloys includes higher Al contents (5-8wt.%) and lower Cr contents (0-13%). Specimens of these alloys are currently being tested, which include the 2nd generation FeCrAl alloys being developed with strengthening additions such as Mo and Si. With a number of samples to evaluate and greater interest in higher temperature capability than 1200°C, a "ramp" test has been used in the past year to provide a faster methodology for evaluating new alloys. Figure 7 shows the temperature profile used in these experiments in the TGA module. When the mass gain increases above ~10mg, typically associated with a rapid increase in the rate, the ramp is stopped and the specimen cooled to room temperature. Not surprisingly, the alloys with 0%Cr began to rapidly oxidize at <700°C, indicating they were not able to form a protective alumina scale. The results for the higher Cr content alloys are currently being collected.

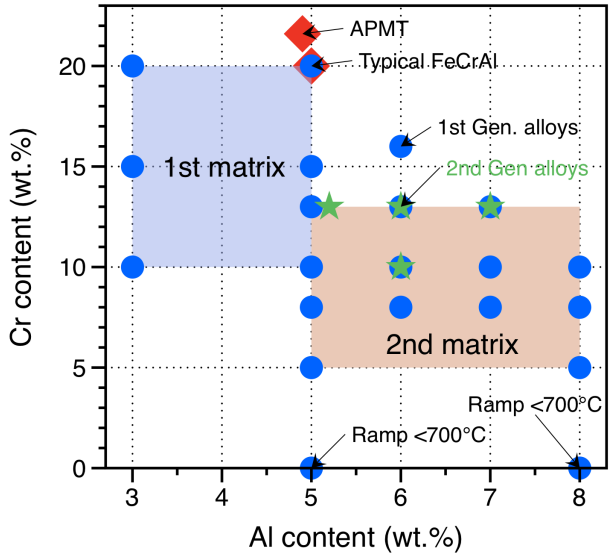

Figure 6. Compositions of first and second test matrices of FeCrAl alloys. The two alloys without Cr failed in the ramp test at <700ºC.

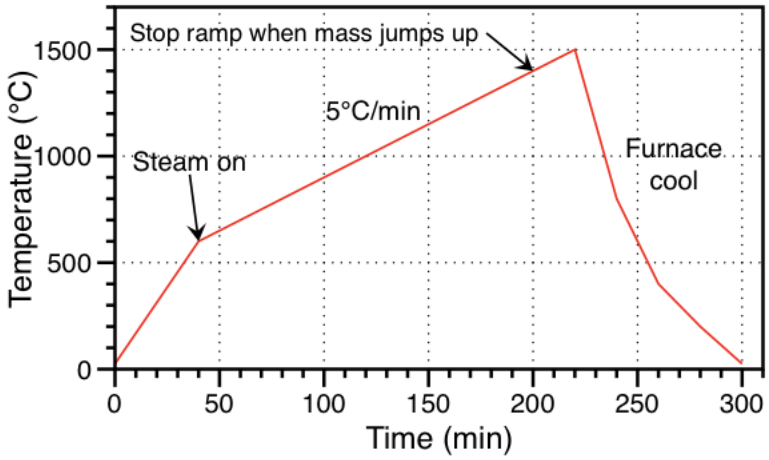

Figure 7. Temperature profile of the "ramp" test in the SATS TGA module.

3. Silica-forming materials.

Again returning to Figure 3, two materials have been evaluated. The MAX phase Ti_3SiC_2 was not able to form SiO_2 in steam at 1200°C and has not been further evaluated. In contrast, high purity SiC form a protective SiO_2 scale with very low reaction rates up to 1600°C. Using the Keiser, high temperature and TGA modules, a wide range of experiments has been completed over a range of temperatures, pressures and flow velocities. For example, Figure 8 shows the effect of temperature on the SiC mass change as a function of temperature. The material recession is governed by paralinear oxidation kinetics that consists of oxide formation and subsequent volatilization. The former is diffusion-limited (parabolic kinetics) and the latter is surface reaction limited (linear kinetics); hence the paralinear kinetics. Although silica volatilizes in flowing steam, the overall recession kinetics remain slow in atmospheric pressures up to ~1700°C, beyond which the oxide layer melts. The oxidation rate accelerates greatly under high-pressure steam conditions (as low as 0.34 MPa) where interconnected defects form in the oxide layer and render it unprotective. Overall, however, even in the high-pressure conditions, the oxidation rate of SiC is well below that of Zr-based alloys, Figure 3.

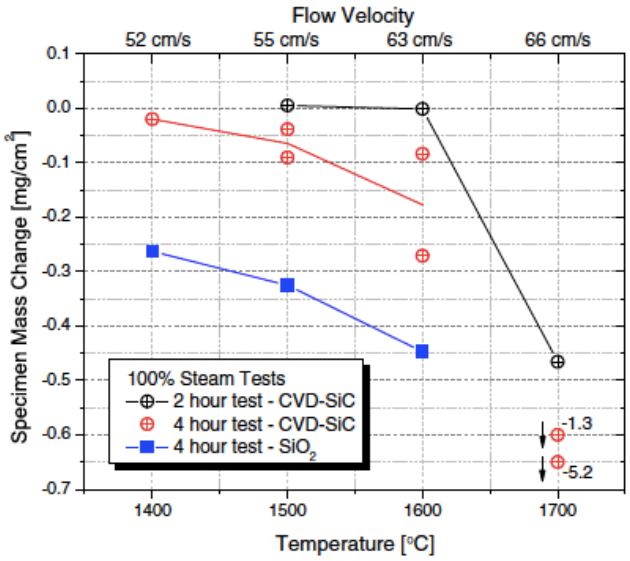

Figure 8. SiC mass change after high-temperature steam exposure under atmospheric conditions.

In addition to these experiments on high-purity SiC, a series of isothermal experiments were completed for Westinghouse on SiC composites at 1300° and 1500°C. The data were provided to Westinghouse for analysis.

4. Molybdenum

Finally, a series of experiments were conducted on commercial La_2O_3-dispersed Mo (MoLX, 0.56%La) provided by EPRI in the high temperature module (to avoid contamination of the TGA module with MoO_3). The results at 700° and 800°C are

shown in Figures 9 and 10. The results are counter-intuitive as the mass loss decreased in steam as the gas velocity increased at both 700° and 800°C. However, in air exposures at 700°C, there was very little effect of gas velocity, Figure 9. Upon reviewing the literature, the results were consistent with the 1963 results of Gulbransen et al. [9] where a competition was identified between MoO_3 formation (mass gain as an oxide forms on the specimen) and evaporation (mass loss as Mo is removed from the specimen) at these temperatures. With a faster flow rate (and a faster supply of O_2 in the steam), more oxide forms on the specimen resulting in less mass loss. At slower velocities, little or no oxide was observed on the specimen and the mass losses were higher.

To address concerns about the O_2 impurity in the steam discussed previously, two more experiments were conducted at 700°C. First, the water was purged with Ar to reduce the O_2 content. Second, the steam was mixed with Ar-4%H_2 to getter oxygen. In both cases, the mass losses were similar to observations in the untreated steam, Figure 7.

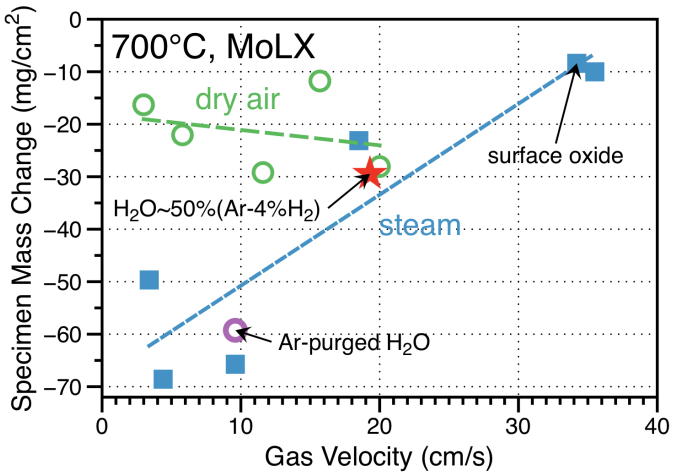

Figure 9. Specimen mass change after 4h exposures of MoLX at 700°C in different flow rates of air, steam and a steam-Ar-4%H_2 mixture.

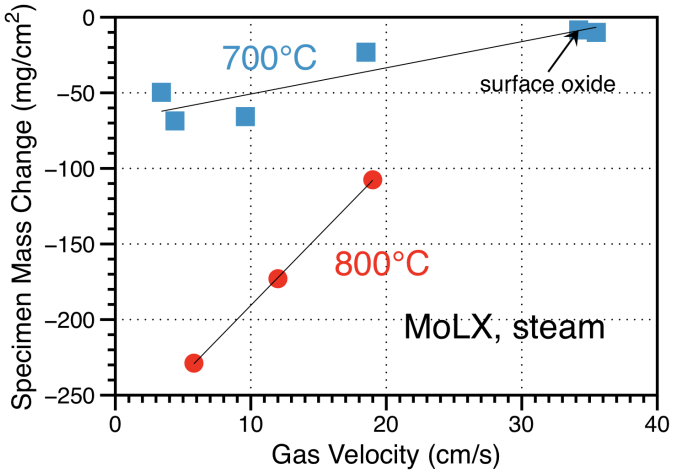

Figure 10. Specimen mass change after 4h exposures of MoLX in steam at different flow rates.

Summary

The high temperature steam oxidation resistance of many different alternative fuel cladding materials has been evaluated in the ORNL severe accident test station over the past 2 years. A number of materials forming chromia, alumina and silica surface oxides are able to form to meet the 100X reduction in oxidation rate compared to Zr-based alloys, which has been defined as the criteria for an accident tolerant fuel system. The most significant current effort is to identify a low-Cr FeCrAl composition where the highest temperature capability of 1475°C steam oxidation resistance is retained.

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