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Steam Oxidation Testing in the Severe Accident Test Station

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B. A. Pint
J. W. McMurray

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Steam Oxidation Testing in the Severe Accident Test Station

B. A. Pint and J. W. McMurray
Oak Ridge National Laboratory, Oak Ridge, TN, 37831

Introduction

Since 2011, Oak Ridge National Laboratory (ORNL) has been conducting high temperature steam oxidation testing of candidate alloys for accident tolerant fuel (ATF) cladding [1-10]. These concepts are designed to enhance safety margins in light water reactors (LWR) during severe accident scenarios. In the US ATF community, the Severe Accident Test Station (SATS) has been evaluating candidate materials (including coatings) since 2012. Compared to the current UO_2/Zr-based alloy fuel system, alternative cladding materials need to offer slower oxidation kinetics and a smaller enthalpy of oxidation in order to significantly reduce the rate of heat and hydrogen generation in the core during a coolant-limited severe accident [11-12]. The steam oxidation behavior of candidate materials is a key metric in the evaluation of ATF concepts and also an important input into models [13-15]. However, prior modeling work of FeCrAl cladding has used incomplete information on the physical properties of FeCrAl. Also, the steam oxidation data being collected at 1200°-1700°C is unique as no prior work has considered steam oxidation of alloys at such high temperatures. In some cases, the results have been difficult to interpret and more fundamental information is needed such as the stability of alumina in flowing steam at 1400°-1500°C. This report summarizes recent work to measure the steam oxidation kinetics of candidate alloys, the evaporation rate of alumina in steam and the development of integral data on FeCrAl compared to conventional Zr-based cladding.

Steam oxidation data

In prior years, the steam oxidation behavior of a wide range of Fe-Cr, Fe-Cr-Al, SiC and MAX phase (e.g. Ti_2AlC) materials were evaluated in the SATS [1-7]. Some current efforts to examine Fe-Cr alloys fall under the collaboration with General Electric (GE) and will not be discussed in this report [10-11]. One new candidate alloy was evaluated this year, Fe-12wt.%Cr-2%Si [16,17]. The Pb-Bi compatibility of this alloy was previously investigated by MIT and Figure 1 shows its performance at 800°-1100°C in 4h exposures in 1 bar steam in the Rubotherm thermogravimetric analysis (TGA) module. With only 12%Cr, this alloy did remarkably well with protective behavior observed up to 1000°C. However, at 1100°C, Fe-rich oxides began to form on the specimen edges resulting in a much higher specimen mass gain. Based on the model Fe-Cr alloy work at ORNL [2,3,6,10], it is possible that a combination of Mo, Mn and Si additions could reduce the required Cr content in a Fe-Cr alloy to lower than 20%. However, recent characterization work of a model Fe-Cr alloy showed that a protective SiO_2 layer did not form at the Cr_2O_3-metal interface after exposure in steam at 1200°C like it did at lower temperatures [10]. Therefore, it is questionable if Fe-Cr alloys could form a protective oxide at temperatures above 1200°-1300°C and be a viable alternative to FeCrAl alloys, which form a more stable α-Al_2O_3 scale and remain protective to ~1500°C in steam. High (>12%) Cr content alloys will be susceptible to α' embrittlement under LWR-relevant irradiation temperature and dose regimes [11,12,18].

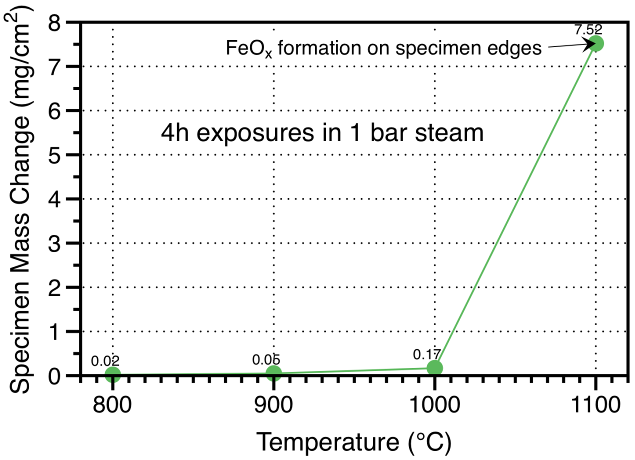


Figure 1. Specimen mass gain during 4h isothermal tests in 1 bar steam at each temperature for specimens of Fe-12Cr-2Si.

Another area that was investigated this year was the behavior of model FeCrAl alloys after exposure to LWR service conditions for 1 year. Ramp testing was performed in 1 bar steam in the TGA on specimens with and without LWR exposures at GE under three different LWR environments [19]. Figure 2a shows the specimen mass gain data during ramp (5°C/min heating rate) testing in 1 bar steam in the TGA. The model Fe-18Cr-3Al+Y specimens all showed low mass gains to 1500°C. Cross-sections of the specimens are shown in Figure 3. The oxide thicknesses are consistent with the post-test specimen mass change data in Figure 2b. Two other alloys also were tested, Figure 2b. However, Fe-13Cr-4Al+Y and Fe-10Cr-5Al+Y are relatively lean compositions (Instead, the commercial tubing compositions are Fe-13Cr-5.5Al and Fe-10Cr-6Al are currently being pursued for fueled cladding irradiation tests). The as-fabricated Fe-13Cr-4Al+Y specimen showed breakaway oxidation during the ramp test as did the specimen of the same alloy exposed in the BWR, H_2 water treatment before exposure. For the Fe-10Cr-5Al+Y specimens, only the specimen exposed to the BWR, O_2 water treatment experienced breakaway oxidation at ~1375°C. The mass changes are summarized in Table 1.

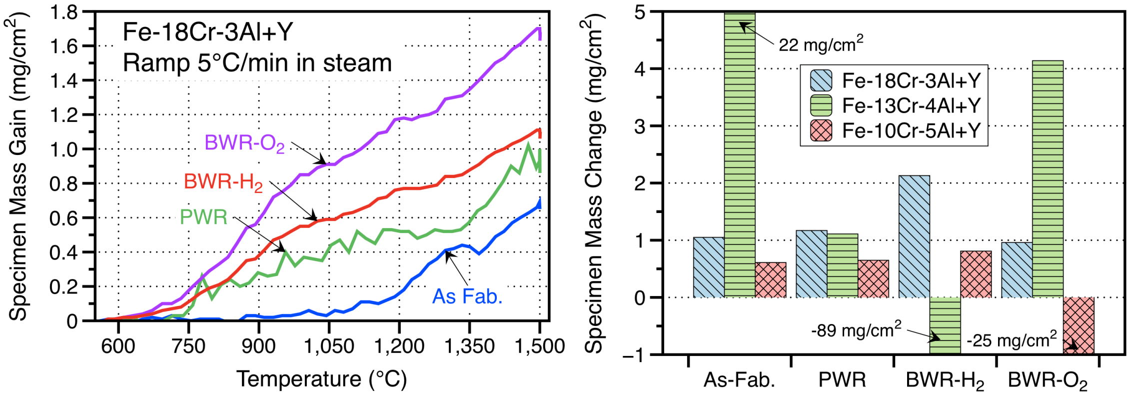


Figure 2. (a) Specimen mass gain during ramp testing in 1 bar steam to 1500°C for Fe-18Cr-3Al+Y specimens with and without 1-year exposure to different LWR conditions, (b) specimen mass change after ramp testing for three different FeCrAl compositions.

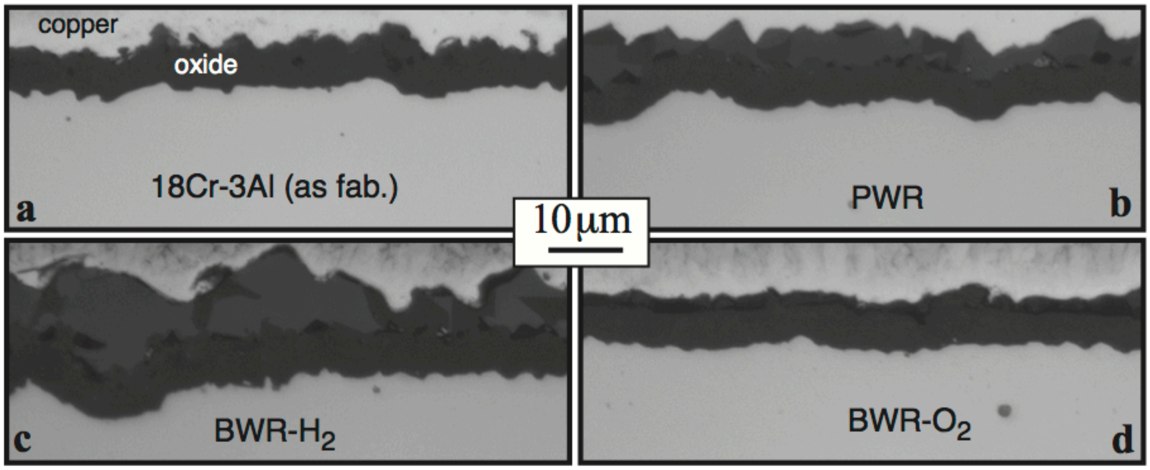


Figure 3. Light microscopy of Fe-18Cr-3Al+Y specimens after ramp testing to 1500°C in 1 bar steam on (a) as fabricated specimen and after a 1-year exposure in (b) PWR, (c) BWR H_2 environment and (d) BWR O_2 environment.

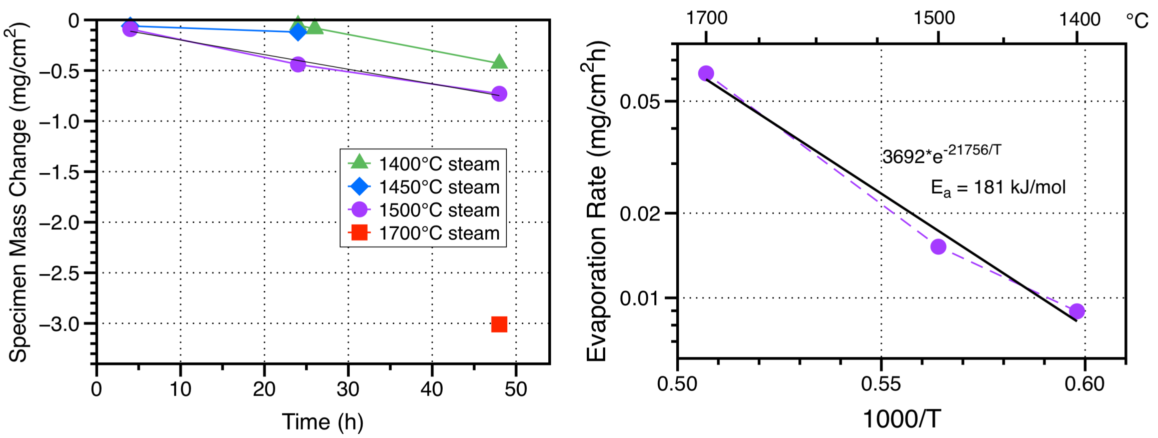
Table 1. High temperature oxidation results for various 1st generation (B) and 2nd generation (C) FeCrAl alloys.

Alloy	As-received (mg/cm^2)	PWR (mg/cm^2)	BWR-H_2 (mg/cm^2)	BWR-O_2 (mg/cm^2)
18Cr-3Al	1.1	1.2	2.1	0.96
13Cr-4Al	22	1.1	-89	4.1
10Cr-5Al	0.61	0.65	0.81	-25

Thus, these results indicate that after extended service in normal operating conditions that FeCrAl cladding would be capable of then forming a protective alumina scale at high temperatures. However, similar testing is needed on the commercial tube alloys to confirm these results on those compositions.

Steam oxidation data

As pointed out in a previous report [20], the steam oxidation resistance of FeCrAl alloys can differ in the TGA and High Temperature SATS modules at ≥1400°C. This difference has been attributed to the possibility of α-Al_2O_3 evaporating in steam at high temperature, which could disrupt its protective behavior. Alumina is known to volatilize as $Al(OH)_3$ under high temperature steam conditions [21]. To further investigate this hypothesis, annealed, high-purity α-Al_2O_3 specimens were exposed in flowing 1 bar steam at ~5 cm/s in the High Temperature SATS module. Figure 4a shows the mass change data obtained. More work is needed to investigate the behavior at 1400° and 1450°C where the mass changes were fairly small. At 1500°C, three exposure times were used in order to confirm linear kinetics (the line fit a power law of n=0.85). Figure 4b shows an Arrhenius plot of the linear evaporation rates measured from the 48h exposures at three temperatures. An activation energy of 181 kJ/mol was determined. The next phase of testing will investigate the evaporation rate as a function of steam velocity and conduct longer exposures at 1400-1450°C where the rates were not as well established. For the typical 4 h experiments run in the SATS, this evaporation does not seem significant enough to disrupt protective scale formation.



(a) (b)

Figure 4. (a) α-Al_2O_3 specimen mass loss as function of exposure time in 1 bar steam at 1400°-1700°C and ~5cm/s, (b) Arrhenius plot of linear evaporation rate based on data in (a).

Integral data collection

In order to collect more accurate physical property data on FeCrAl alloys, a series of experiments were conducted that also have been reported elsewhere [22]. First, the solidus temperature was determined by using a differential scanning calorimeter/thermogravimetric analysis (DSC-TGA) instrument. Figure 5 shows a contour plot of the solidus temperature as a function of alloy Cr and Al contents. The DSC-TGA temperature was calibrated by melting pure standards. The map is based on 6 measurements of model alloys and CALPHAD calculations. Similar experiments were conducted on FeCrAl specimens that were fully oxidized to Fe-rich oxide. Figure 6 shows example DSC-TGA data from the oxide formed on Fe-15Cr-15Al+Y tested in Ar-20%O_2. The temperature, mass change (%) and DSC results are shown. For a fully-oxidized FeCrAl coupon, the specimen consisted of two oxide phases: $(Fe,Cr)_3O_4$ and $(Fe,Cr)_2O_3$. A clear decomposition of $(Fe,Cr)_2O_3$ to $(Fe,Cr)_3O_4$ was observed (mass loss of 2.74%) the first time the specimen was heated above 1500°C. The specimen was repeatedly cycled from 1500°-1700°C with no indication of melting. Similar results were found with other oxide specimens.

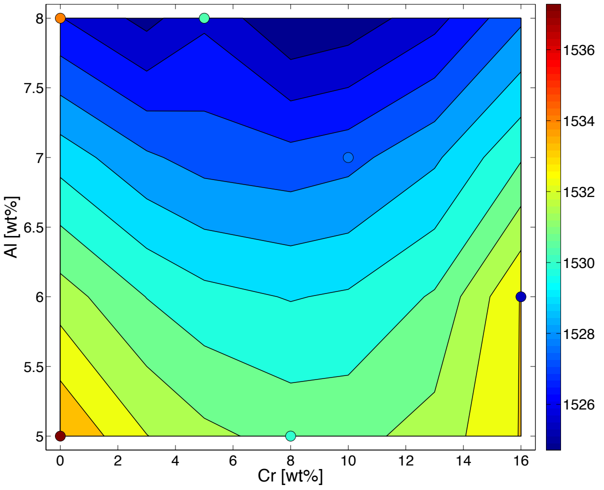


Figure 5. Solidus temperature for FeCrAl alloys as a function of Cr and Al contents [22].

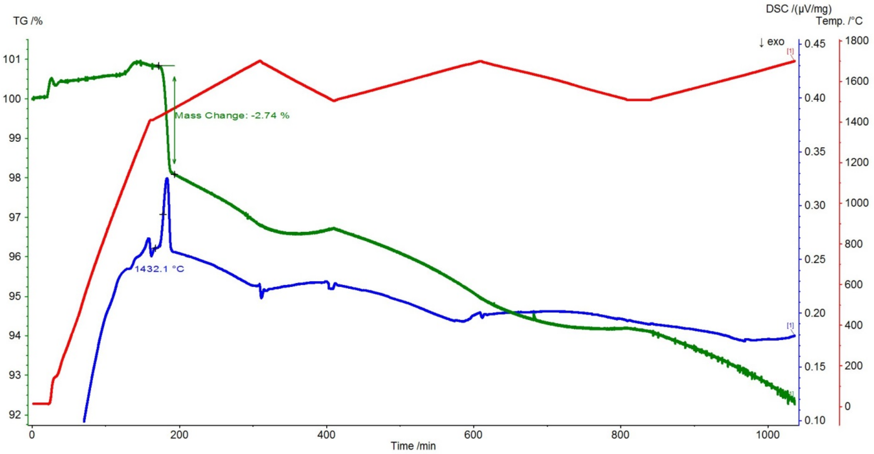


Figure 6. DSC-TGA data for a fully oxidized Fe-15Cr-15Al+Y specimen [22].

Steam oxidation testing of tube specimens was conducted at 1400°-1700°C to compare the behavior of a Zr-based alloy, Zircaloy-4 (Zr-4), and FeCrAl, particularly to see how the FeCrAl tubing would perform above its melting temperature (Zircaloy tubing is known to undergo cracking and loss of any notable strength, though it retains its shape after oxidizing to ZrO_2 [22]). The initial testing was conducted with the tube in a crucible and an alumina rod inside the tube to simulate the fuel, Figures 7a and 7b. Figures 8a and 8b show Zr-4 and commercial Fe-10Cr-6Al+Mo,Si,Y (C06M) tubing after 1h testing in steam at 1400°C, respectively. While C06M performed well at 1400°C, it experienced melting in both a ramp test to 1500°C and a 1700°C 1h exposure, Figures 8c and 8d. This first phase of testing raised several concerns. First, the specimen was shielded from the steam flow in the high temperature SATS module by the crucible, Figure 7b. Second, it was difficult to see the specimen degradation inside the crucible, Figure 8d. Third, with a 1h hold time, it was not possible to determine if the melting happened during ramping to the test temperature or sometime during the 1h hold. Thus, the second phase of testing was conducted in the holder shown in Figure 7c with the tube still with an alumina rod inside but now exposed to the steam flow and visible after exposure. An alumina "catch pan" was added to prevent debris from falling into the bottom of the furnace (far right in Figure 7c). Finally, the specimen was ramped to temperature in ~90 min with an Ar purge to 600°C when the steam was introduced. After reaching temperature, the specimen was held for ~1 min before

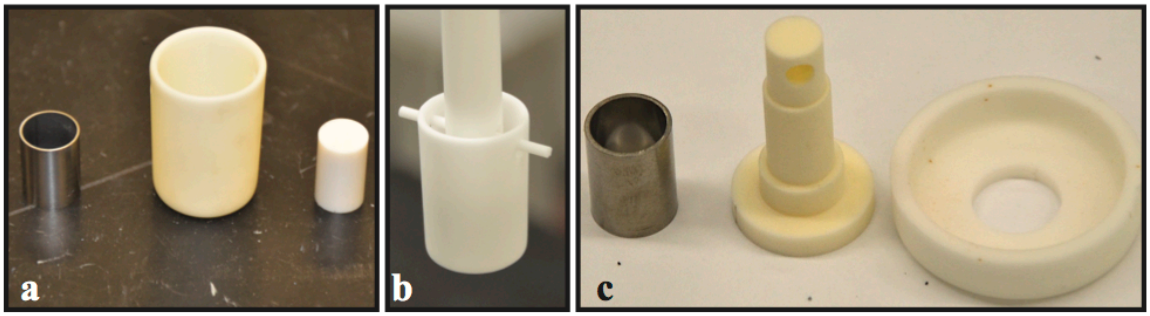


Figure 7. Specimen holders for tube testing: (a) tube specimen with alumina cylinder inside tube assembled as in (b) and (c) shows the holder used for the majority of testing.

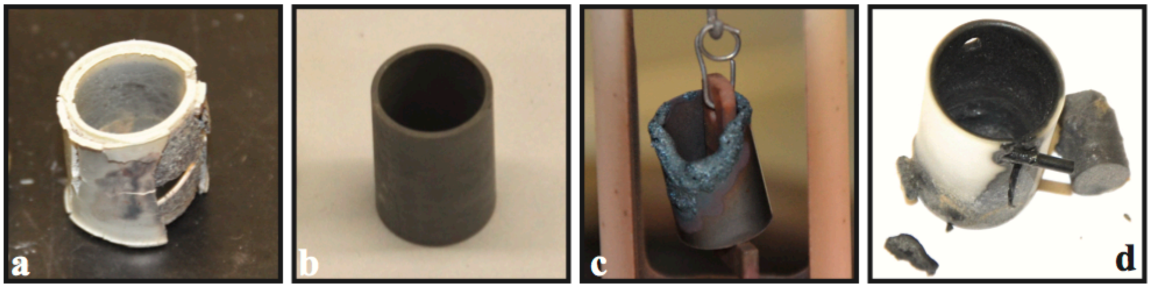


Figure 8. Tube specimens after testing in 1 bar steam (a) Zircalloy-4 tubing exposed for 1h at 1400°C (b) commercial Fe-10Cr-6Al+Mo,Si,Y tubing after the same exposure, (c) commercial Fe-10Cr-6Al+Mo,Si,Y tubing after ramp testing to 1500°C and (d) commercial Fe-10Cr-6Al+Mo,Si,Y tubing after 1h at 1700°C.

cooling to room temperature. Comparison experiments were conducted in dry air to examine the role of steam at these high temperatures.

Figure 9 shows the Zr-4 tube specimens after exposures in air and steam from 1400°-1700°C. In most cases, the Zr-4 tubing held its shape up to 1700°C despite being fully oxidized to ZrO_2, consistent with the models. There appeared to be little difference between oxidation in 1 bar air or steam, although there appeared to be more spallation in steam, contrary to a previous study that indicated more severe degradation in air [23]. Figure 10 shows similar exposures for commercial Kanthal alloy APM performed to date. This alloy was used as the commercial low-Cr FeCrAl tubing was in short supply at the time these experiments were conducted. As expected, the APM tube specimens survived testing to 1400° and 1500°C in steam and air with the formation of a relatively thin surface oxide. However, the APM specimen exposed in steam at 1600°C did begin to slump after exposure. Additional exposures up to 1700°C are in progress.

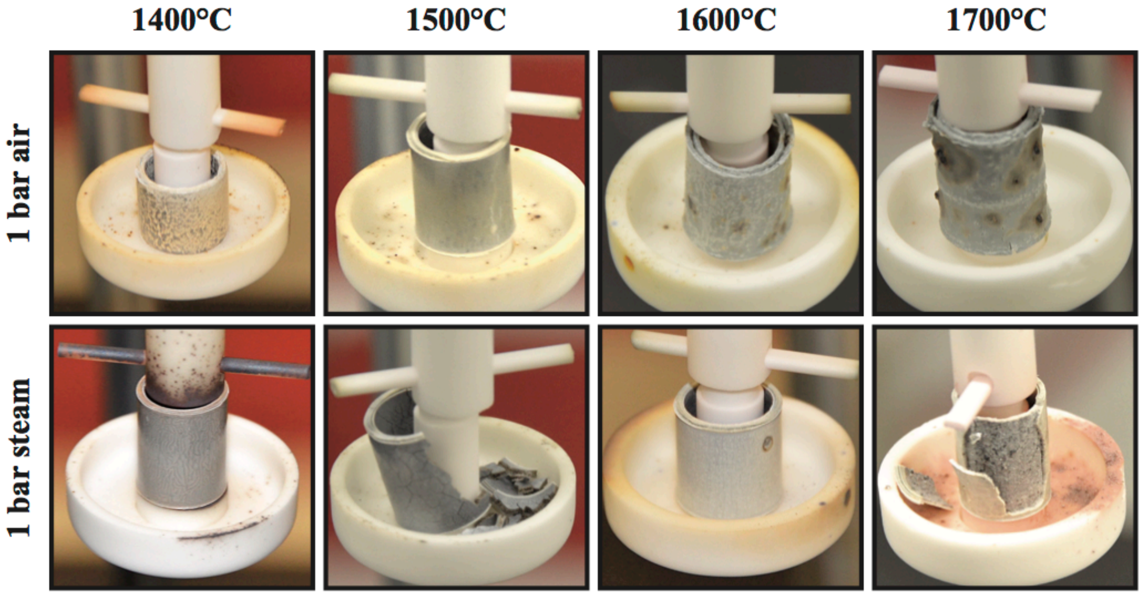


Figure 9. Comparison of commercial Zircalloy-4 tubing after exposures to various temperatures in 1 bar air or steam.

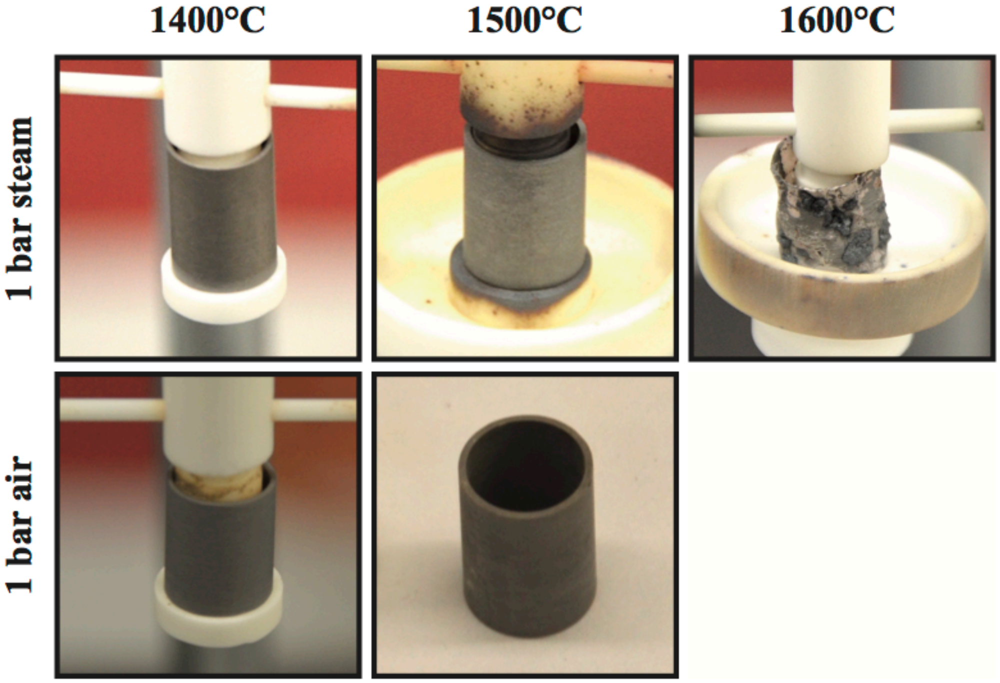


Figure 10. Comparison of commercial APM (FeCrAl) tubing after exposures to various temperatures in 1 bar air or steam.

Summary

Over the past several years, the high temperature steam oxidation resistance of many different alternative fuel cladding materials has been evaluated in the ORNL SATS. New candidates continue to be evaluated, such as Fe-12Cr-2Si. However, additional aspects of steam oxidation behavior are now being investigated. For example, the ramp testing behavior of model FeCrAl alloys to 1500°C in steam was compared to specimens of the same alloy ramp tested after 1 year exposures to LWR conditions at 280°-330°C. The evaporation behavior of alumina in steam at 1400°-1700°C also is being investigated to gain a more fundamental understanding of the steam oxidation behavior of FeCrAl at ≥1400°C. Finally, to assist in modeling of FeCrAl cladding, DSC-TGA experiments are being conducted to study the melting behavior of FeCrAl alloys and Fe-rich oxides. In addition, air and steam exposures of Zr-4 and APM tubing also are being conducted at 1400°-1700°C to understand how FeCrAl tubing will behave after rapid oxidation occurs. As more commercial FeCrAl tubing becomes available in the coming months, these types of experiments will be repeated on that material to confirm these results and assist in the development of accurate predictive models for accident scenarios with more accident tolerant fuel claddings.

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