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FY–17 FCRD Milestone M3FT-17OR020202111
Steam Oxidation Testing in the Severe Accident Test Station

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Introduction

After the March 2011 accident at Fukushima Daiichi, Oak Ridge National Laboratory (ORNL) began conducting high temperature steam oxidation testing of candidate materials for accident tolerant fuel (ATF) cladding in August 2011 [1-11]. The ATF concept is to enhance safety margins in light water reactors (LWR) during severe accident scenarios by identifying materials with 100× slower steam oxidation rates compared to current Zr-based alloys. In 2012, the ORNL laboratory equipment was expanded and made available to the entire ATF community as the Severe Accident Test Station (SATS) [4,12]. Compared to the current UO_2/Zr-based alloy fuel system, an ATF alternative would significantly reduce the rate of heat and hydrogen generation in the core during a coolant-limited severe accident [13-14]. The steam oxidation behavior of candidate materials is a key metric in the evaluation of ATF concepts and also an important input into models [15-17]. However, initial 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. Also, because many accident scenarios include steadily increasing temperatures, the required data are not traditional isothermal exposures but exposures with varying "ramp" rates. In some cases, the steam oxidation behavior has been surprising and difficult to interpret. Thus, more fundamental information continues to be collected. In addition, more work continues to focus on commercially-manufactured tube material. This report summarizes recent work to characterize the behavior of candidate alloys exposed to high temperature steam, evaluate steam oxidation behavior in various ramp scenarios and continue to collect integral data on FeCrAl compared to conventional Zr-based cladding.

Steam oxidation behavior

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 using the SATS platform [1-11]. In the previous report [18], initial results were presented on Fe-12wt.%Cr-2%Si, which was previously investigated for improved Pb-Bi compatibility at MIT [19,20]. In 4 h isothermal exposures in steam, protective behavior was observed at 800°-1000°C, but a large mass gain was observed at 1100°C (7.5 mg/cm^2). Figure 1a shows the thin, Cr-rich oxide formed at 1000°C, while a voluminous Fe-rich oxide formed at 1100°C, Figure 1b. The specimen with the thin oxide was Cu-plated prior to sectioning to protect the scale. These results were consistent with concurrent work with General Electric (GE) [10] where 22-25%Cr levels were need for protective behavior at 1200°C in steam. The addition of 2%Si appeared to have a significant benefit in terms of steam oxidation resistance and further work is expected with higher Cr alloys. Figure 1c shows a follow up result with a model Fe-25Cr-0.67Mn-0.25Si alloy exposed for 4 h at 1200°C in steam. High (>12%) Cr content alloys will be susceptible to α′ embrittlement under LWR-relevant irradiation temperature and dose regimes [12,13,21].

Another area that was investigated this year was the effect of Y on the high temperature performance of FeCrAlY. Several previous model alloys contained relatively low Y contents (30 ppmw) and underwent significant spallation after isothermal exposures at >1200°C. Two new alloys B106Y2 (9.7Cr-6.1Al-0.14Y) and B125Y2 (11.6Cr-5.1Al-0.17Y) were fabricated with

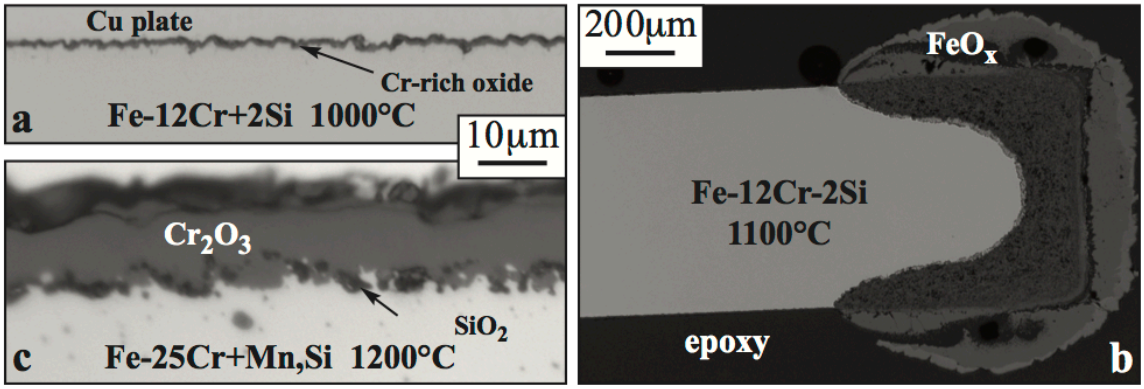

Figure 1. Light microscopy of specimens exposed for 4h in steam: Fe-12Cr-2Si (a) at 1000°C and (b) 1100°C, (c) Fe-25Cr-1Mn-0.3Si at 1200°C.

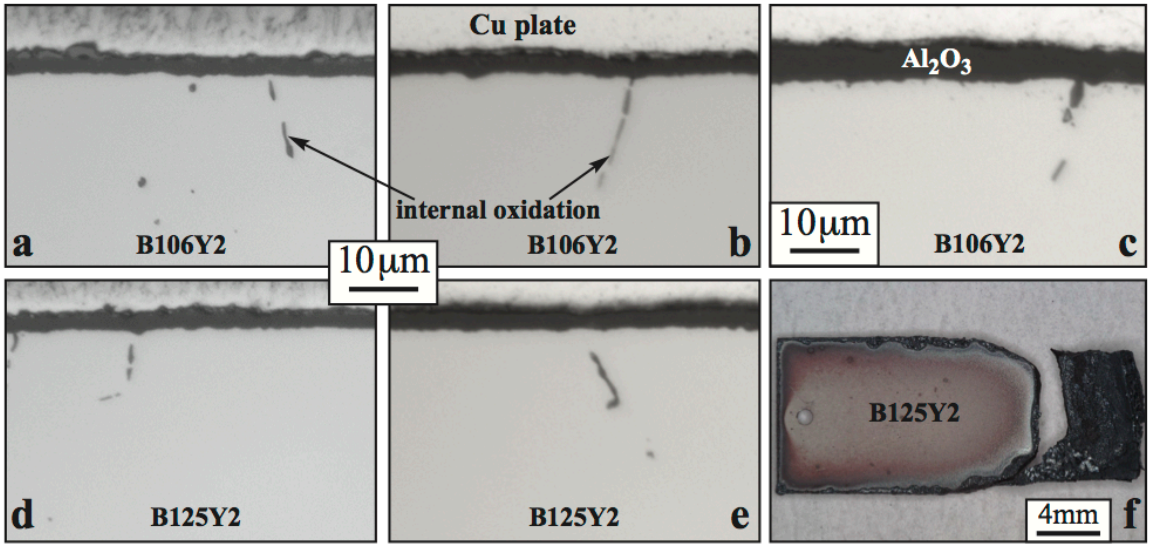

Figure 2. Light microscopy of B106Y2 (a-c) and B125Y2 (d-f) specimens after exposure to steam for (a,d) 4 h at 1200°C, (b,e) 1 h at 1300°C and (c,f) 1 h at 1400°C.

higher Y contents (800-1000 ppma) to determine its impact. Figure 2 summarizes the results at 1200°-1400°C. At 1300° and 1400°C, the exposures were for only 1 h, while the 1200°C exposure was 4 h. With the higher Y content, some internal oxidation was evident in all of the polished cross-sections in Figure 2. However, the new alloys did not perform significantly better than the previous versions of these compositions. Figure 2f shows that the B125Y2 specimen exposed at 1400°C could not completely form a protective alumina scale and experienced rapid FeO_x formation, similar to B125Y. The comparison of these two compositions indicates the importance of higher Al contents for ≥1400°C oxidation behavior when the Cr content is lowered to 10-13%.

Integral data collection: Ramp testing of tube specimens

As commercially fabricated FeCrAl tubing has become available, more of the experiments have focused on tube specimens, ~12mm long and 9.5mm diameter. The majority of work explored several ramp and hold scenarios based on various accident scenarios shown in Table 1 [22]. The tube specimens were mainly B136Y (13Cr-6Al) with a few comparisons made to commercial

Table 1. Summary of various ramp and hold times investigated.

1st rate (°C/min)	Temperature (°C)	Hold (min)	2nd rate (°C/min)	Maximum Temp.
12	1200	50	11.1	1400-1500°C
16.67	1412	1	4.17	1500°C
7.4	1182	1	1.81	1500-1550°C
5.7	1108	1	1.57	1500°C

Kanthal alloy APMT (21Cr-5.5Al) tubing. Under the scenarios in Table 1, specimens were first heated to 600°C at 20°C/min where the steam was introduced. The first ramp rate was then used to heat the specimens to an intermediate temperature followed by a second ramp to a maximum temperature. For the first scenario with heating to 1200°C at 12°C/min, the specimens were held for 50 min before the second ramp. Figure 3 shows the final mass gain after stopping at various temperatures for the B136Y tubes. The specimens formed thin protective alumina scales in steam to a maximum temperature of 1450°C. At higher temperatures, the specimens rapidly oxidized. Figure 4 shows cross-sections of the various B136Y tube specimens. The specimen in Figure 4a was ramped to 1200°C and then cooled to room temperature in flowing argon, while the specimen in Figure 4b was ramped and held for 50 min before cooling. Figure 4c and 4d show the thin protective scale formed after ramps in steam to 1400° and 1450°C, respectively. Figures 4e and 4f show the specimens that were fully oxidized after ramping to 1475° and 1500°C, respectively. Figure 3 also notes that an APMT specimen exposed using the same protocol was able to remain protective after exposure to 1500°C. Thus, dropping the Cr content from ~21wt.% to 13% resulted in a ~50°C drop in the maximum temperature capability.

The B136Y tube specimens from the three other ramp sequences are shown in Figure 5. The first specimen at each condition was stopped after the first ramp and the second specimen was continued to 1500°C. In this case, using a slower ramp rate to 1500°C, all specimens survived exposure up to 1500°C. For the 16.67°C/min ramp rate, the specimen heated to 1412°C is shown in Figure 5a. Figure 5b shows a second specimen that continued to 1500°C. A similar pairing for the 7.4°C/min heating rate is shown in Figure 5c and 5d. Figure 5e shows the

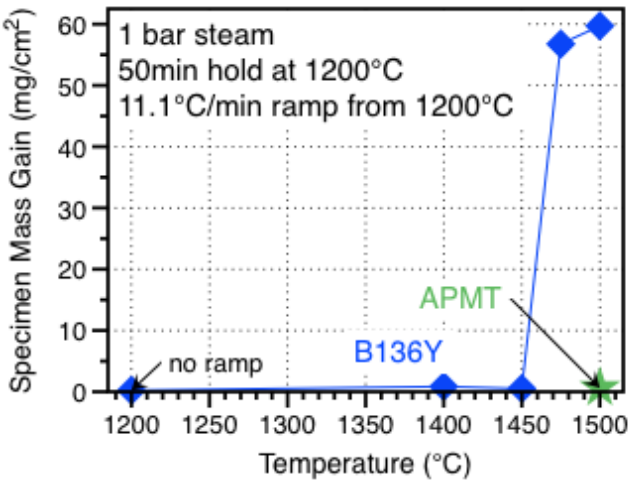

Figure 3. Specimen mass gain after holding for 50min at 1200°C followed by ramping to temperatures above 1200°C at 11.1°C/min.

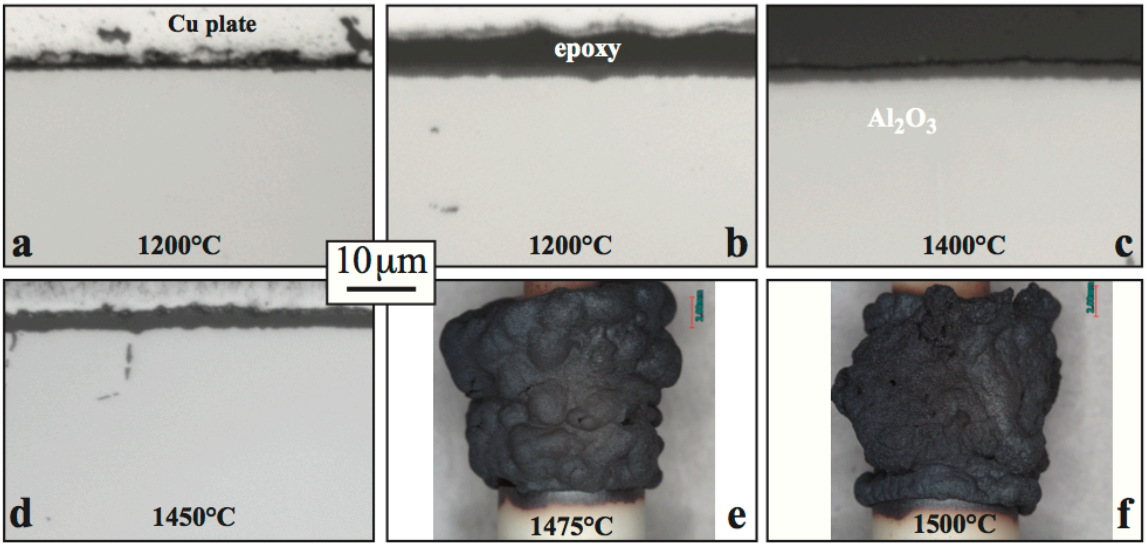

Figure 4. Light microscopy of B136Y tube specimens exposed to steam up to various temperatures with a 12°C/min heating rate to 1200°C and a 11.1°C/min heating rate above 1200°C (a) 1200°C 1 min hold, (b) 1200°C, 50 min hold, (c) 1400°C, (d) 1450°C, (e) 1475°C and (f) 1500°C.

specimen heated to 1108°C at 5.7°C/min and stopped. It was not sectioned because of the low temperature and expected thin oxide formed. Figure 5f shows the specimen like in Figure 5e that was subsequently heated to 1500°C at 1.57°C/min (>4 h ramp time). Based on the success of the slower heating rates in going to higher temperatures (compared to the results in Figure 3), an

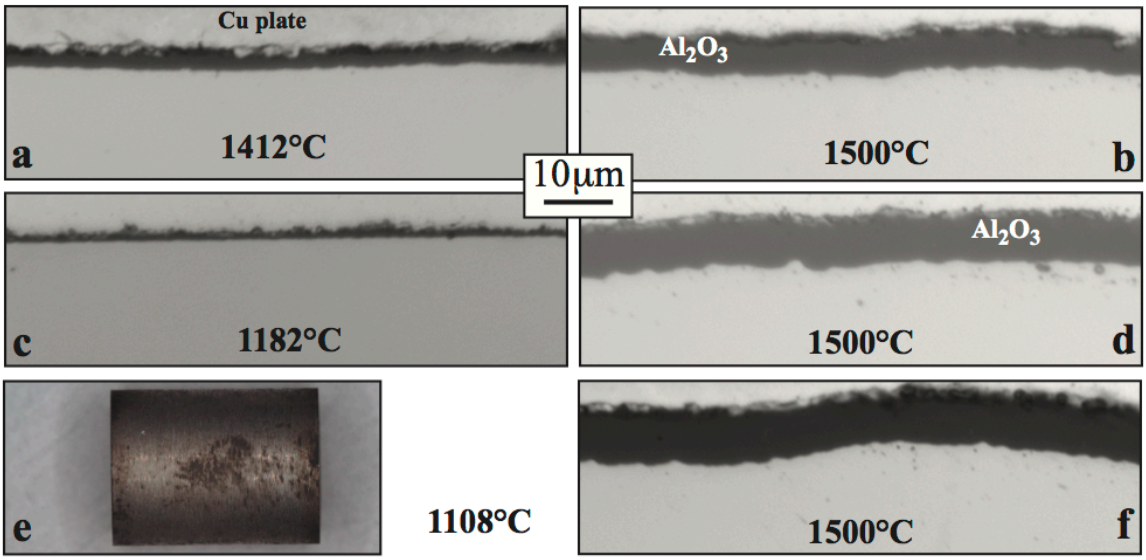

Figure 5. Light microscopy of B136Y tube specimens exposed to steam up to various temperatures (a) 16.67°C/min heating to 1412°C, (b) like (a) followed by ramping to 1500°C at 4.17°C/min, (c) 7.4°C/min heating to 1182°C, (d) like (c) followed by ramping to 1500°C at 1.81°C/min, (e) 5.7°C/min heating to 1108°C, (f) like (e) followed by ramping to 1500°C at 1.57°C/min. The specimens were Cu-plated prior to sectioning to protect the alumina scale.

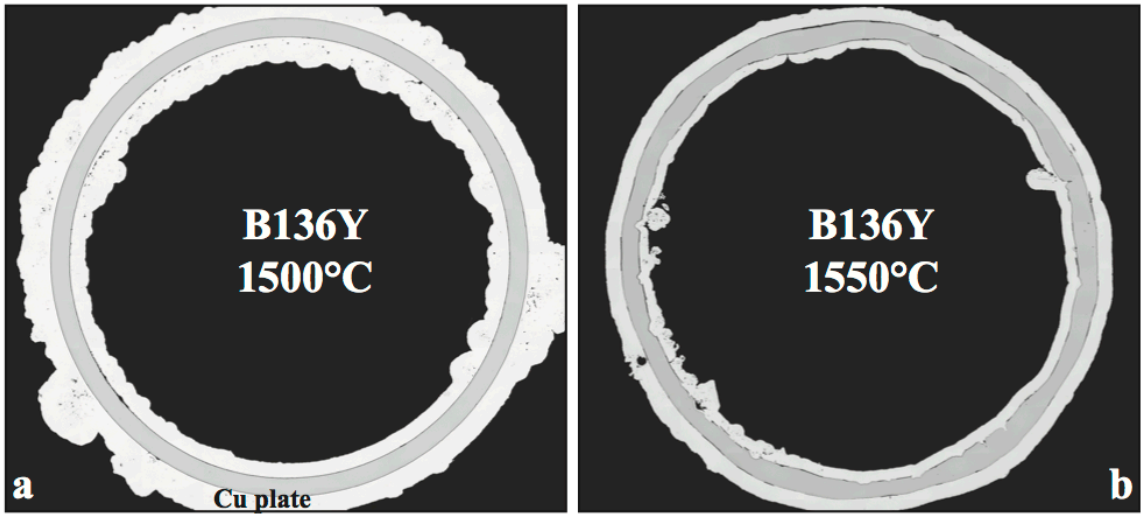

Figure 6. Light microscopy of the B136Y tube specimens (a) same specimen as shown in Figure 5d and (b) using same ramp rate (1.81°C/min) heated to 1550°C.

additional B136Y tube specimen was continued to 1550°C after first heating to 1182°C at 7.4°C/min followed by heating at 1.81°C/min to 1550°C. Remarkably, the specimen was not fully consumed and the specimen measured very little mass change. However, Figure 6 compares the cross-sections of the specimens heated to 1500°C and 1550°C. The specimen stopped at 1500°C is the same one shown at higher magnification in Figure 5d. While that specimen retained its wall thickness and diameter, the specimen heated to 1550°C appears to have slightly deformed and has a non-uniform wall thickness. This suggests that the specimen may have been above the solidus temperature. Several aspects are still being evaluated. First, that the alumina scale may have helped support the structure above the liquidus temperature and second, that the loss of Al due to selective oxidation may have depleted the alloy sufficiently to increase the liquidus temperature. However, the melting point for pure Fe is only 1538°C. Therefore, another aspect that needs to be verified is the accuracy of the specimen thermocouple.

Integral data collection: interaction assessments

Finally, initial experiments have begun to assess the interactions of FeCrAl (B136Y sheet specimens) with other alloys in the reactor core. Initial tests were performed on bare, polished alloy coupons in flowing argon using a 1h hold at temperature. The specimens were placed in the bottom of an alumina crucible with an alumina cylinder on top to ensure good contact was maintained throughout the exposure, Figure 7. The results are summarized in Figure 8 as very minimal interaction was observed. The initial test matrix was to expose FeCrAl with and without a pre-oxidation step. However, because of the limited interaction observed without pre-oxidation, the pre-oxidation experiments were skipped. The minimal interaction contrasts with the behavior of Zr-based alloys which form low melting point eutectics with Fe and Ni at <1000°C [23]. Additional experiments are planned with B_4C.

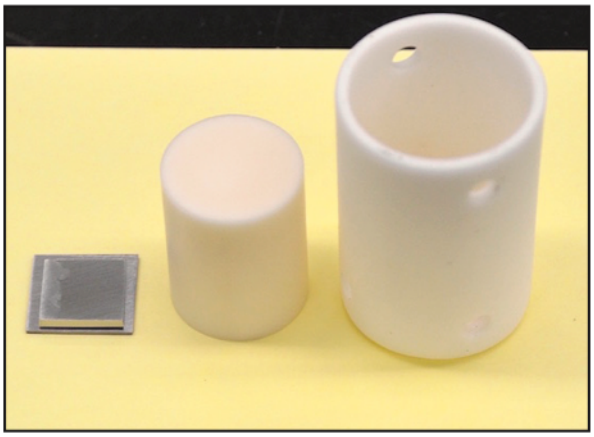

Figure 7. Specimen holders for the interaction testing. The alumina cylinder (center) was placed on top of the metal specimens during heating in the alumina crucible in the high temperature furnace.

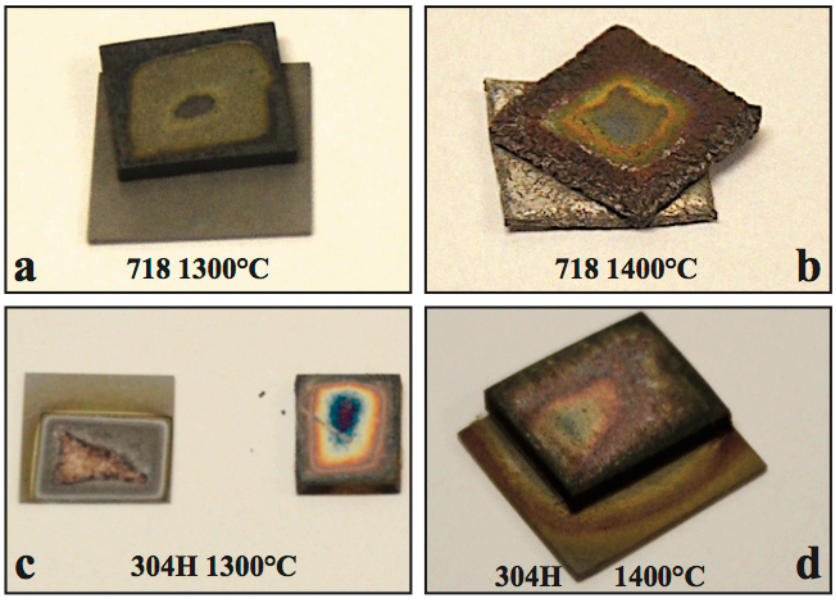

Figure 8. Interaction test results for FeCrAl (B136Y) sheet (1.5cm x 1.5cm) with alloy 718 coupon for 1h at (a) 1300°C and (b) 1400°C and with type 304H stainless steel coupon (c) 1300°C and (d) 1400°C. Polished (bare) specimens were exposed in flowing argon.

Summary

Since 2011, the high temperature steam oxidation resistance of many different alternative cladding materials has been evaluated in the ORNL SATS. New candidate alloys continue to be evaluated such as Fe-12Cr-2Si, which performed substantially better than Fe-Cr alloys with less Si. Additional aspects of steam oxidation of FeCrAl alloys at 1400°-1550°C are being explored, primarily to evaluate commercial tube specimens and provide data to develop and validate models. Numerous exposures were conducted using commercially-fabricated B136Y (13Cr-6Al) tubing. Comparing various ramp rates, the slower rates to 1500°C permitted the formation of a

protective alumina scale to 1500°C whereas a faster rate (11.1°C/min) resulted in complete oxidation of the specimen after ramping to only 1475°C. Finally, recent integral tests have included alloy interaction experiments between FeCrAl (B136Y) sheet and Ni-base alloy 718 and type 304H stainless steel at 1300° and 1400°C in argon. Very little interaction occurred after exposure despite having polished metal surfaces in contact.

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