PERFORMANCE OF IRON-CHROMIUM-ALUMINUM ALLOY SURFACE COATINGS ON ZIRCALOY 2
UNDER HIGH-TEMPERATURE STEAM AND NORMAL BWR OPERATING CONDITIONS

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Abstract

Iron-chromium-aluminum (FeCrAl) coatings deposited on Zircaloy 2 (Zy2) and yttria-stabilized zirconia (YSZ) by magnetron sputtering have been tested with respect to oxidation weight gain in high-temperature steam. In addition, autoclave testing of FeCrAl-coated Zy2 coupons under pressure-temperature-dissolved oxygen coolant conditions representative of a boiling water reactor (BWR) environment has been performed. Four different FeCrAl compositions have been tested in 700 °C steam; compositions that promote alumina formation inhibited oxidation of the underlying Zy2. Parabolic growth kinetics of alumina on FeCrAl-coated Zy2 is quantified via elemental depth profiling. Autoclave testing under normal BWR operating conditions (288 °C, 9.5 MPa with normal water chemistry) up to 20 days demonstrates observable weight gain over uncoated Zy2 simultaneously exposed to the same environment. However, no FeCrAl film degradation was observed. The 900 °C eutectic in binary Fe-Zr is addressed with the FeCrAl-YSZ system.

Keywords: LWR cladding, oxidation, corrosion, protective coatings, FeCrAl, alumina

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1. Introduction

The 2011 Fukushima Dai-ichi accident prompted world-wide effort to improve light-water reactor (LWR) fuel performance with respect to Zircaloy cladding oxidation in steam during off-normal temperature transients [1-3]. High-temperature steam exposure, a consequence of post-transient low-pressure core re-flooding, results in rapid oxidation of Zr-based cladding, additional heat generation (Zr oxidation is exothermic), hydrogen gas generation, and the consumption of ductile metal in favor of a brittle metal oxide. All of these phenomena are potentially detrimental to maintaining coolable core geometry and prohibiting radionuclide dispersal. The overall goal of our work is to demonstrate that rapid oxidation during high temperature steam exposure associated with temperature transients is reduced or eliminated by the FeCrAl coating.

Recent work has primarily focused on two solution pathways to mitigate cladding oxidation during high-temperature steam exposure: i) the development of oxide-resistant bulk monolithic cladding materials such as silicon carbide composites [4-7], ternary iron-chromium-aluminum (FeCrAl) alloys [8-10], and molybdenum [11], and ii) oxide-resistant coatings on monolithic Zr-based cladding [12, 13]. Advantages and disadvantages exist for all solutions. Here we examine the performance of FeCrAl coatings on Zircaloy 2 (Zy2) under high-temperature steam and normal boiling water reactor (BWR) conditions.

Oxidation studies of Zr-based cladding material in normal LWR operational environments [14, 15] and in high-temperature steam have spanned many decades [15, 16] and continue to be an active area of research [17, 18]. Generally, the oxidation of Zr-based alloys follows a parabolic rate law above ~1000 °C characteristic of a protective or well-adhering oxide layer. A quasi-cubic response that eventually leads to breakaway (linear kinetics) oxidation associated with a non-protective oxide layer occurs in both steam and LWR coolant conditions at lower temperature [14, 17].

The response of monolithic FeCrAl to oxidizing conditions has been studied in high-temperature steam for LWR applications [8, 9] and in high-temperature oxidizing environments for other industrial applications [19-25]. Monolithic FeCrAl is not susceptible to substantial oxidation or corrosion at high temperature due to the formation of a protective alumina oxide scale. Weight-gain and/or thickness-consumed measurements during high-temperature steam exposure of FeCrAl demonstrate improved oxidation susceptibility compared to Zr-based alloys, with parabolic rate constants reduced by orders of magnitude [3, 9]. A minimum Al concentration of ~3 percent by weight (wt %) within the ternary FeCrAl matrix is required to promote a continuous alumina scale during dry air exposure [20]. Chromia formation is known to be effective as well, but not to the same extent as alumina [3, 9]. A minimum Cr concentration in excess of ~20 wt % is necessary to promote a protective chromia oxide scale during high-temperature oxidation. This is demonstrated by a comparison of 304 (~19 wt % Cr)

and 310 (~25 wt % Cr) stainless steel weight gain and parabolic rate constant measurements in high temperature steam [3, 9].

The experimental procedures used to grow and characterize the FeCrAl films used in this study, the methods for high-temperature steam and normal BWR condition exposure, and the microanalytical techniques to characterize the post-exposure response of the films are presented in the next section. Weight gain measurements, analysis of the oxidation products using X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), and elemental depth profiles from Auger Electron Spectroscopy (AES) comprise the primary results presented in Section 3. Discussion will focus on correlations between oxidation resistance, film composition, and elemental depth profiles. Summary statements are then made.

2. Experimental Approach

2.1 *FeCrAl film growth and microanalytical characterization*

FeCrAl films were grown on polished Zy2 and yttria-stabilized zirconia (YSZ) by magnetron sputtering using a system described previously [26]. The Zy2 rolled sheet material was supplied by ATI Specialty Alloys and Compounds. This recrystallized material had nominal Zy2 composition for LWR applications, was β -quenched, and was supplied at thicknesses of 1.5 mm. The epi-polished YSZ substrate material was supplied by MTI Corporation. Four FeCrAl film compositions (Fe/Cr/Al atomic percent of 53/29/18, 62/4/34, 71/7/22, and 86/10/4) were grown by single or co-deposition from FeCrAl sputter targets with specified atomic compositions of 53/29/18, 62/4/34 and 86/10/4. The sputter targets were supplied by AJA International. Ultra-high purity (UHP) Ar was used as the sputter gas at typical pressures of 0.5 Pa. Sputter growth was done in current-control mode with target power levels of 70 to 110 W. The Zy2 substrates were mechanically polished on both faces, with the final polishing step using a 0.05 μm silica suspension. The YSZ substrates were single-side epi-polished to 0.5 nm roughness, a standard specification for epitaxial growth. All FeCrAl films were grown at 300 °C; typical growth rates were 0.15 nm/s and a 1 μm thick film required approximately 2 hours of deposition time. Film thicknesses were calibrated with cross sectional scanning electron microscopy (SEM) analysis of films grown under identical conditions on single crystal Si substrates. The suite of samples used in this study are listed in Tables 1 and 2, which includes sputter deposition conditions, steam/water exposure conditions, and the microanalytical analysis techniques used to characterize the films. Samples are designated below with the following notation: substrate-Al composition-exposure temperature-exposure time so that Zy2-34Al-700C-10h is a FeCrAl coating on Zy2 with a Fe/Cr/Al:62/4/34 composition exposed to steam at 700 °C for 10 hours.

The as-grown and post-exposure FeCrAl films were characterized by SEM, scanning transmission electron microscopy (STEM), XRD, AES, and SEM/EDS. AES provides elemental

composition as a function of depth. The secondary electron detection channel of SEM provides near-surface topographical information and XRD was used to determine crystal lattice structure.

Two SEM instruments were used in this work, a Hitachi S4700 high resolution SEM and a JEOL 6060LV general purpose SEM. The Hitachi S4700 SEM uses a cold field emission gun to achieve 1.5 nm resolution at 15 kV and was equipped with an Oxford instrument ISIS EDS X-ray Microanalysis System. The JEOL 6060LV SEM uses a pre-centered W hairpin filament and has a spatial resolution of 3.5 nm at 30 kV. This instrument can be operated in a low vacuum mode, useful for analyzing non-conducting samples. This instrument is also equipped with an Oxford Instrument ISIS EDS system. A JEOL 2010F STEM instrument was used to study the structure and chemical composition of post-exposure FeCrAl on Zy2 at nanometer level using a 0.2 nm beam. This instrument operates at 200 kV and uses a Schottkey field emitter source. Atomic number or Z-contrast images of a lifted out cross section specimen were obtained. The system is capable of EDS using an Oxford INCA 30mm ATW detector. A Physical Electronics PHI 660 AES system was used for chemical depth profiling. Typical operating parameters were to use either 3 or 5 keV electrons, electron currents of 150 to 200 nA, and 3 keV Ar sputter ions over a 500 by 500 μm^2 raster area. The analytical electron beam was 300 by 300 nm^2 centered on the sputter raster area. Evidence of porosity is presented below that becomes significant at long exposure times (hours) in steam. All AES depth profiles were performed far from the pores. An Al foil mask with a 1 mm diameter hole was used to prevent charge buildup and sputter re-deposition. Two Panalytical/Philips X'pert MRD systems were used for crystal lattice structure determination. These instruments have fixed Cu anodes. One of these diffractometers has high-resolution capability with Cu K- α_2 rejection. Both ω -2 θ specular scans and glancing-angle ($\omega \sim 2^\circ$) 2 θ scans of as-grown and post-exposure films were performed under ambient conditions.

2.2 High-temperature steam and LWR coolant exposure

A commercial NEITZCH Jupiter 441 Simultaneous Thermal Analyzer (STA) with a water vapor generator was used for high-temperature steam exposure. This system allows isothermal weight gain measurements under inert and steam environments with an operational (during 700 °C steam exposure) accuracy of order 10^{-2} mg. For reference, mass gains are of order 10^0 to 10^2 mg were typically observed during high-temperature steam exposure. UHP Ar carrier and protective gases were used to minimize non-steam oxidation. All internal and external carrier and protective gas handling hardware were stainless steel. This system also has absolute differential scanning calorimetry capability. This capability along with internal thermocouple temperature sensors were calibrated using the solid-liquid melting reactions of various metals. Samples were heated in flowing Ar at a rate of 15 °C/min to the desired exposure temperature. Steam was introduced at a rate of 2 gm/hr after an isothermal equilibration hold period of 20 minutes. Background runs without a sample to correct for buoyancy were performed with

identical time-temperature-steam characteristics for all measurements. Typically, some weight gain on uncoated Zircaloy 2 ($\sim 5 \text{ g/m}^2$, see below) was observed during sample heating and the equilibrating hold, indicating unavoidable oxidation due to the highly reactive properties of Zr. Samples were exposed to steam at 700, 1100, and 1250 °C for periods from 30 minutes to 15 hours.

Nine flat, $10 \times 10 \text{ mm}^2$, 1.5 mm thick coupons coated on both surfaces with a 1.3 μm thick Fe/Cr/Al:62/4/34 atomic composition were exposed to a simulated BWR environment in a Ni-based alloy autoclave. These samples are listed in Table 2. This environment consisted of 288 °C water at a pressure of 9.5 MPa with normal water chemistry (NWC) of 2ppm dissolved oxygen (DO). The total duration of the exposure was up to 20 days, with a subset of samples removed after 10 days of exposure. The FeCrAl film integrity was maintained throughout the autoclave test based on post-exposure visual inspection and SEM analysis.

3. Results and Analysis

3.1 Weight-gain measurements of FeCrAl films on Zy2

Weight-gain measurements in 700 °C steam were performed on a series of FeCrAl films with different compositions. These measurements are presented in Fig. 1A as weight gain normalized to the total sample surface area. All samples were coated on both faces, with the specimen edges receiving partial FeCrAl film coverage and therefore responding more like uncoated Zy2. Three compositions (Fe/Cr/Al 53/29/18, 62/4/34, and 71/7/22) resulted in significantly lower normalized weight gain compared to uncoated Zy2. The fourth composition, 86/10/4 (or 88/10/2 weight percent) has a poor oxidation response, consistent with the Al and Cr concentration minima [3, 9] discussed in the Introduction. The normalized weight-gain data for the coated samples have been corrected for the effect of incomplete coverage of the edges. This correction was made by subtracting the measured uncoated Zy2 response multiplied by the (estimated) fractional area of the coated sample edges. The FeCrAl samples presented in Fig. 1A were small, with areal dimensions of $\sim 2 \times 5 \text{ mm}^2$. The rollover observed at long times in Fig. 1A is the result of sample oxidation reducing the available surface area. The uncoated Zy2 correction to the FeCrAl-Zy2 coated samples scales inversely with the surface area. A large area $10 \times 10 \text{ mm}^2$ FeCrAl sample (Zy2-34Al-700C-3.7h) was exposed to 700 °C steam to minimize the effect of this correction.

The two compositions with higher Al concentration performed equally well and one (62/4/34) was chosen to test the response of a large-area FeCrAl two-side deposition. The response of Zy2-34Al-700C-3.7h is shown in Figure 1B. The response of an uncoated Zy2 (Zy2-00Al-700C-10h) with similar dimensions was measured as well and compared to Zy2-34Al-700C-3.7h. We present the Zy2-34Al-700C-3.7h data as a weight-gain band; the lower limit of this band corresponds to the area-weighted subtraction of the uncoated Zy2 response,

while the upper limit corresponds to the measured weight gain without any Zy2 subtraction. The true response, with partial FeCrAl coverage of the edges, lies between these two limits. The rollover associated complete oxidation does not occur for the larger uncoated Zy2 sample in Figure 1B. We note for comparison the measurements of the FeCrAl industrial alloy Kanthal AF by Götling *et al.* in O₂+steam at 900 °C [23]; normalized weight gains of order 10⁻¹ g/m² were observed after ~2 hours. This indicates the true response of our FeCrAl film is closer to the lower limit of the shaded band in Figure 1B.

The slope of normalized weight gain versus time is proportional to the power from the exothermic oxidation reaction. The two end-of-run slopes in Fig. 1B differ by a factor of five, demonstrating the effectiveness of the FeCrAl coating with respect to heat generation rate. The ratio of these slopes could in fact be much larger if the lower limit of the weight gain band for Zy2-34Al-700C-3.7h closer to the actual FeCrAl response.

3.2 XRD analysis of as-grown and exposed FeCrAl films on Zy2 and YSZ substrates

FeCrAl-YSZ represents a model system because 1) the low-temperature (~900 °C) eutectic in the binary Fe-Zr system is not present, 2) zirconia or possibly YSZ are potential barrier layers to prevent the Fe-Zr eutectic reaction at elevated temperature in the FeCrAl-Zircaloy system, 3) XRD analysis is not complicated by multiple substrate reflections, and 4) microanalytical analysis is not influenced by interdiffusion across the film-substrate interface since YSZ is very stable with respect to mass transport at elevated temperature [26]. On the other hand, the oxidation products created during high-temperature steam exposure may not necessarily be representative of those for the FeCrAl-Zircaloy system. Further, Fe(Cr)-Zr intermetallic phase formation occurs in the FeCrAl-Zircaloy system [8] but is eliminated with YSZ.

XRD analysis of as-grown and exposed FeCrAl films on YSZ is shown in Figure 2. All FeCrAl-YSZ films investigated with XRD had atomic concentrations of Fe/Cr/Al:62/4/34. The as-grown FeCrAl film (YSZ-34Al-000C-00h) has a primitive cubic (Pm-3m) unit cell based on the ω -2 θ specular scan presented in Figure 2. The Pm-3m unit cell corresponds to the FeAl solid solution phase. The film is highly textured since the strong Pm-3m (110) reflection is absent in the specular scan. Textured growth is expected on a single crystal substrate. 700 °C steam exposure of FeCrAl films with significant Al content leads to alumina formation at the free surface. Aluminum segregation to the free surface to form alumina depletes the balance of the film. The consequence of this is a lattice structure change from primitive cubic to an Fe-based BCC (Im-3m) structure. This structural change manifests in the specular scan of exposed YSZ-34Al-700C-3.5h as the elimination of the (100) reflection, forbidden for the BCC lattice, and (211) reflection intensity, otherwise absent (but not forbidden) in the primitive cubic pattern. Alumina reflections were not observed due to the relatively small volume of this phase and the fact that specular scans were performed in high-resolution mode. Alumina reflections were observed with glancing-angle XRD analysis of the exposed FeCrAl-Zy2 samples.

1100 °C steam exposure (YSZ-34Al-1100C-2.5h in Fig. 2) results in reflections consistent with FeAl_2O_4 spinel structure or a spinel with some degree of inversion. More importantly, the 900 °C Fe-Zr binary eutectic reaction did not occur during 1100 °C (or 1250 °C, not presented here) steam exposure. Otherwise, reflections from the FeCrAl film, a spinel, or other oxide structures would not have been observed. This was in fact the case with 1100 °C steam exposure of the FeCrAl-Zy2 system; melting and evaporation associated with the binary eutectic lead to complete film loss and normal Zy2 oxidation kinetics (Zy2-34Al-1100C-0.5h in Table 1). We note the weight gain for all FeCrAl-YSZ samples was zero within the accuracy of the STA, as expected since FeCrAl does not readily oxidize and YSZ is stable in oxidizing environments. This observation implies the Zy2-34Al-700C-3.7h weight gain shown in Fig. 1B is largely due to Zy2-like oxidation of the uncoated edges. If this is the case, the *lower* limit of the shaded band is representative of the true response.

Glancing-angle XRD scans of as-grown and FeCrAl films on Zy2 exposed to 700 °C steam (Zy2-34Al-700C-0.5h and Zy2-34Al-700C-10h) are compared to the specular scan of as-grown Zy2-34Al-000C-00h in Figure 3. As with the as-grown FeCrAl-YSZ deposition, as-grown Fe/Cr/Al:62/4/34 on Zy2 is primitive cubic. The Zy2 substrate is a polycrystalline template, leading to a polycrystalline FeCrAl film and a more powder-like XRD pattern. Glancing-angle diffraction geometry was used to increase the near-surface sensitivity and minimizes the substrate reflection peak intensity. Reflections from the 0.5 hour exposed sample can be indexed to the primitive cubic FeAl or α -alumina; Zr-matrix intensity has been completely eliminated by the glancing-angle geometry. Prolonged, 10 hour exposure has resulted in consumption of FeCrAl and the formation of α -alumina and a $\text{Cr}_2(\text{FeAl})$ intermetallic phase (Fd-3m) that was observed with AES. The Al-oxide is indexed as α -alumina in Figure 3. However, many different Al oxides phases exist with significant overlap of diffraction intensity [27] and this indexing should not be considered conclusive.

XRD analysis of the autoclave-testing coupons is compared to the as-grown Zy2-34Al-000C-00h sample in Figure 4. Glancing-angle diffraction geometry was again used to increase near-surface sensitivity of the exposed sample. All reflections can be indexed to the Zr matrix, primitive cubic phase corresponding to the as-grown FeCrAl, the Fe_3Al BCC phase discussed above, and the NiFe_2O_4 spinel. The precipitation of this spinel phase is expected for long-term exposure in a Ni-based alloy autoclave. The weight gain per unit area for these autoclave exposures are shown in Figure 5. One face of two of the coated samples was scratched prior to autoclave exposure to create a galvanic cell. The presence of these scratches had no effect of the overall weight gain or localized NiFe_2O_4 spinel precipitation. Four uncoated Zy2 specimens simultaneously exposed are also included in Figure 5. No film degradation was observed based on post-exposure visual inspection. The FeCrAl-Zy2 system performance in normal BWR operational conditions, at least up to 20 days, is therefore deemed adequate.

3.3 Elemental analysis and surface topography from AES and SEM/EDS

AES depth profiles of as-grown and post-steam-exposure FeCrAl films with atomic composition of 62/4/34 are shown in Figure 6. The post-700 °C steam exposure profiles exhibit a near-surface stoichiometry consistent with alumina formation. Alumina is observed to grow into the film as the exposure time increases; analysis of this trend is presented in the next section. Significant interdiffusion of Fe, Al, and Zr across the original film-substrate interface is observed in the AES depth profiles, with the development of a FeZr_2 intermetallic compound consistent with SEM observations by Terrani *et al.* [8]. The loss of Al from the FeCrAl film to the Zr matrix would eventually terminate alumina growth. A barrier layer such as zirconia would impede interdiffusion. Similar alumina near-surface stoichiometry was observed in AES analysis of the FeCrAl-YSZ system for both 700 and 1100 °C steam exposure but is not shown.

We note two additional aspects of the AES profiles. The first is the tendency for Cr to segregate just below the alumina layer at long exposure time. The combined expulsion of Cr from the alumina layer and the lack of significant Cr diffusivity into the substrate results in a segregation peak. The second is the ability of the alumina layer on thicker FeCrAl films to inhibit *zirconia* growth. Zirconia formation is not observed after 15 hours of exposure (Fig. 6H). However, an exposure of 20 hours (Fig. 6G) does lead to zirconia formation.

Extended depth profiles of Zy2-34Al-700C-15h (600 nm FeCrAl coating) and Zy2-34Al-700C-10h (300 nm FeCrAl coating) exposed to 700 °C steam for 15 and 10 hours, respectively, in Figure 7. We also include the AES depth profile for Zy2-4Al-700C-15h, the low Cr/Al composition FeCrAl film. The lack of alumina formation on this sample (Fe_2O_3 forms instead) and significant zirconia growth is consistent with the poor oxidation protection and associated weight gain observed for this composition in Figure 1A. Oxygen-Zr stoichiometry consistent with zirconia persists to depths of microns, followed by stoichiometry consistent with the α -Zr-O solid solution phase in Figs. 7A-7D. We cannot conclusively establish that the zirconia formation is correlated to initial FeCrAl thickness and subsequent alumina layer thickness, although this appears to be the case. We also note the tendency for greater Fe segregation in the thinner films, as opposed to Cr segregation in the thicker films (compare Fig. 6G and Fig. 7C). This is attributed to lower total Cr inventory in thinner films and the lack of significant diffusivity of cation impurities (Fe, Cr, and Al) into ionic ZrO_2 . The latter observation leads us to believe zirconia could be effective diffusion barrier and prevent the Fe-Zr eutectic reaction.

The as-grown film composition determined in AES analysis (Fig. 6A) does not agree with the sputter target composition (Fe/Cr/Al:62/4/34), over-predicting the Fe concentration relative to Al. This is the result of the preferential sputtering of Al during AES analysis. Preferential sputtering is a well-studied phenomenon and perturbs the near-surface composition of solid solutions to depths equal to the penetration depth of the incident ion (~3 nm in our case for a 3 keV Ar AES sputter ion beam) [28]. The deposition of FeCrAl films using magnetron sputtering depletes Al in the near-surface region of the *sputter target*. However, the steady state flux of

sputtered atoms must equal to the target composition based on atomic conservation. We therefore expect as-grown film composition equal to sputter target composition. Sputter erosion associated with AES depth analysis of the FeCrAl films depletes the near-surface region of Al as well. The steady-state sputtered atom yield during AES analysis is also equal to the target composition. However, AES analysis does not quantify sputter atom yield, but instead measures the surface composition with an electron analytical beam that induces the emission of Auger electrons. Energy spectroscopy is performed on the Auger electrons to determine elemental species. Auger electrons have escape depths of 1 to 5 nm, overlapping with the ~3 nm depletion region; AES analysis is therefore most sensitive to the depletion layer created by preferential sputtering associated with depth profile analysis.

The as-grown and post-steam-exposure surface morphologies of the FeCrAl-Zy2 system are shown in Figure 8. A columnar grain structure is evident in the cross section SEM image of the as-grown film, with a plan-view grain size of approximately 200 nm. Porosity is evident in samples with high Al concentration exposed to 700 °C steam. Similar features were observed post-exposure of FeCrAl films on YSZ but are not shown. Cross sectional SEM presented below demonstrates the formation of pores (as opposed to surface pitting) between the alumina scale and the underlying material. Porosity has also been observed after high-temperature oxidation of FeCrAl [23, 24]. A cracked, poorly-adhering Fe₂O₃ oxide scale formed on FeCrAl samples with low Al and Cr (86/10/4), as is evident in Figure 8F. This observation is consistent with the poor oxidation response for Zy2-4Al-700C-15h in Figure 1A.

Additional cross-section STEM analysis of Zy2-34Al-700C-10h (300 nm thick FeCrAl film) is shown in Figure 9. This analysis demonstrates porosity develops below the alumina layer within the original FeCrAl film and that alumina layer is prone to cracking. The thickness of the zirconia growth front (~3 μm) is quantified as well. We note this thickness agrees reasonably well with the AES depth profile for the same sample (Fig. 7B).

Two plan-view post-exposure SEM images of the Zy2 autoclave coupons are shown in Figure 10. The post-exposure surface of the coated coupons is characterized by the precipitation of the NiFe₂O₄ spinel. The uncoated samples (not shown) exhibited uniform corrosion with no significant surface topological features in plan-view SEM.

The final SEM/EDS elemental analysis we present is YSZ-34Al-1100C-2.5h in Figure 11. As mentioned above, the FeCrAl-YSZ system is not subject to the low temperature Fe-Zr binary eutectic and the effect of higher temperature steam exposure can be studied. Two distinct surface oxide morphologies are observed for this sample, flaky and granular regions. The result of elemental composition analysis of these two regions (20 keV incident electron beam) is listed in Table 3 and indicates the former is Fe-rich and the latter is Al-rich. We note neither EDS or AES are sensitive to hydrogen and the possibility of hydroxides [Fe(OH)₂ or Fe(OH)₃] cannot be excluded. The composition of the regions 1 and 2 are consistent with the formation of an AB₂O₄ spinel. The oxygen and total cation concentrations are as expected for a spinel, 4/7~0.6 and

3/7~0.4, respectively, per formula unit. The compositions for regions 1 and 2 appear to reflect a Fe- and Al-spinels, respectively, with some degree of inversion; B cation mixing on the tetrahedral and octahedral sites in both regions must occur since the minor A cation concentration is below 1/7~0.14. More important is the fact that the FeCrAl film was not lost to the eutectic reaction during 1100 °C steam exposure, but instead reacted with steam to form spinel phases.

4. Discussion

4.1 Alumina growth kinetic analysis

700 °C steam exposure of FeCrAl films with high Al concentration promotes alumina formation that significantly inhibits oxidation of the base metal. We have not performed a systematic study of the effect of Al concentration with regard to alumina formation. However, the film composition with the lowest Al concentration (2% by weight) did not perform well, consistent with the study FeCrAl oxidation in dry air by Engkvist *et al.* [20]. Our approach was to select one composition that did perform well with respect to weight gain (the Fe/Cr/Al:64/4/34 composition) for extensive study.

We confirm parabolic alumina growth kinetics during 700 °C steam exposure from AES depth profiles and show this analysis in Figure 12. The growth kinetics we observe are faster than that observed from the high temperature steam exposure of APMT (a commercial FeCrAl alloy) from Pint *et al.* [9], with a parabolic rate constant K_p a factor of ~8 larger. The layer thickness scales with the square-root of K_p and the alumina oxide thicknesses we observed here are a factor of ~3 greater than AMPT. However, the temperature range investigated by Pint *et al.* was much higher and relatively narrow (1000 to 1200 °C) [9]. There are two important consequences of this limited range. First, extrapolation of the Pint *et al.* Arrhenius K_p behavior to 700 °C can potentially introduce error since small changes in the slope (proportional to the effective activation energy) lead to large deviations. Second, the possibility exists that the lower temperature range is characterized by a different effective activation energy, which would invalidate the extrapolation of the Pint *et al.* high-temperature K_p behavior to 700 °C.

We note the alumina growth kinetics in dry O₂ observed by Josefsson *et al.* between 500 and 900 °C [25]. This is one of the few FeCrAl oxidation studies below 800 °C and the kinetic response obeys an Arrhenius response, although this analysis was not published by Josefsson *et al.* We compare the Pint *et al.* [9] and Josefsson *et al.* [25] alumina parabolic rate constants to our own in Table 4. We also use these responses to calculate the alumina layer thickness Δx for a 6 hour 700 °C exposure and compare this to our value measured with AES (sample Zy2-34Al-700C-6h). The effective diffusion constant D_o and activation energy E_a characterizing the Josefsson *et al.* Arrhenius behavior is at variance with those of Pint *et al.* This is an indication

alumina growth is influenced by environmental factors such temperature and steam versus dry O₂.

4.2 Alumina growth kinetic error estimation and calibration

Alumina growth rates based on AES depth profiles have potential sources of systematic error. The depth scale is determined by setting the film-substrate interface to the original film thickness from the cross section SEM image (Fig. 8A). However, the post-exposure interface is blurred due to interdiffusion, especially for long exposure times. The film-substrate interface is assumed to be the Fe-Zr cross over point (0.5 to 10 hour exposure times) or the half-Zr signal depth (15 hour exposure time) in the AES depth profiles. The alumina layer thicknesses determined in the Fig. 6 profiles also assume constant sputter rates from the free surface to the base substrate, but the sputter rates for alumina and the metal phases are likely unequal. Finally, the observed porosity will influence the sputter erosion rate down to the original FeCrAl-Zy2 interface (Figs. 9A and B indicate pores do not extend into the base metal substrate) and this will introduce a non-linearity to the depth scale, especially for the high porosity observed for long exposures. As stated above, pores were avoided by the analytical beam, but not necessarily by the sputter beam, especially at high porosity. Alumina growth rates based on mass gain of monolithic material are not influenced by these issues. However, we cannot rely on mass gain since oxidation of uncoated Zy2 is always present to some extent.

We have attempted to calibrate the alumina depth scale by performing profilometer measurements of AES sputter craters terminated at the alumina-Fe/Cr interfacial depth for six and 10 hour Zy2-34Al-000C-00h exposure samples. Sub-micron profilometer measurements of sputter craters are also problematic, but we show these as two additional data points in Figure 12. We determine the parabolic rate constant for alumina growth based on the profilometer measurements and list this value in Table 4 as well. The profilometer K_p has greater uncertainty but is in better agreement with the Pint *et al.* result. This indicates our AES depth scale may result in slightly conservative alumina growth rates.

4.3 Alumina effectiveness to mitigate Z-coated oxidation

We can use both the AES profiles (Figs. 6 and 7) and STEM analysis (Fig. 9) to determine the effectiveness of alumina formation in prevent zirconia formation—the overall goal of the FeCrAl coating. An estimate for the zirconia layer thickness for *uncoated* Zy2 can be obtained from the Fig. 1 Zy2-00Al-700C-15h normalized weight gain data for comparison; $\sim 4 \times 145 \text{ [g}\cdot\text{m}^{-2}] / 5.7 \text{ [g}\cdot\text{cm}^{-3}] \sim 100 \text{ }\mu\text{m}$ after 10 hr exposure, where the factor of 4 accounts for the oxygen mass ratio in the ZrO₂ formula unit. This can be compared to the zirconia thickness from the Fig. 7B AES profile ($\sim 3.5 \text{ }\mu\text{m}$) or the zirconia thickness from STEM analysis ($\sim 3 \text{ }\mu\text{m}$). The effect of alumina growth is to impede the $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2(\text{g})$ reaction in 700 °C steam by

about a factor of ~ 33 ($\sim 3 \mu\text{m}$ versus $100 \mu\text{m}$). This is a conservative estimate since the Zy2-34Al-700C-10h FeCrAl film in Figs. 7B and 9 was 300 nm.

The AES profile shown in Fig. 6H reveals a $\sim 1.5 \mu\text{m}$ zirconia layer after 20 hour steam exposure (the approximate ZrO_2 composition is observed between 25 and $40 \mu\text{m}$) for an 1100 nm FeCrAl film. (Note that the Fig. 6H AES measurement was extended to greater depths and indicated Zr(O) solid solution beyond $40 \mu\text{m}$.) If we assume linear breakaway oxidation kinetics for uncoated Zy2, a $\sim 200 \mu\text{m}$ zirconia layer would form at 20 hours. We can then estimate the effect of an 1100 nm FeCrAl coating as a factor of ~ 130 reduction of zirconia formation during 700°C steam exposure. The effectiveness therefore scales linearly with FeCrAl thickness.

4.4 FeCrAl coating lattice structure and microstructural changes

XRD analysis of as-grown Fe/Cr/Al:64/4/34 on both YSZ and Zy2 shows a primitive cubic (Pm-3m) structure with reflections indexed to FeAl, an intermetallic compound with extended solid solution solubility [29]. The difference between this lattice structure and the Fe_3Al BCC (Im-3m) structure is the presence of the forbidden (100) reflection. This reflection occurs in as-grown films on both YSZ and Zy2. AES analysis of the as-grown film indicates a $\text{Fe}_{1+x}(\text{AlCr})_{1-x}$ compound with $x \sim 0.5$; in other words, $\text{Fe}_3(\text{AlCr})$. However, AES does not provide structural information and we consider XRD analysis more definitive proof of the FeAl primitive cubic Pm-3m phase. Furthermore, AES over-predicts Fe concentration. 700°C steam exposure of the FeCrAl-Zy2 system and associated alumina growth reduced the Al concentration within the balance of the film. This leads to a Pm-3m $\rightarrow$ Im-3m lattice structure change within the FeCrAl film that is demonstrated by XRD analysis of the FeCrAl-YSZ system.

The formation of spinel phases during high-temperature steam exposure (1100°C) of the FeCrAl-YSZ system is confirmed by the XRD response and is supported by EDS analysis of the flaky and granular oxide products. AES depth profile analysis (not shown) demonstrated each region had invariant composition to the YSZ interface, with compositions consistent with EDS analysis. This system demonstrates the utility of YSZ (and perhaps zirconia) to eliminate the Fe-Zr eutectic reaction that resulted in complete film loss during 1100°C steam exposure of the FeCrAl-Zy2 system.

The AES depth profiles of Zy2-34Al-700C-15h and Zy2-34Al-700C-10h demonstrate zirconia can act as an effective barrier for cation transport. However, the stability of zirconia with respect to the dissolution of oxygen to form $\alpha\text{-Zr-O}$ solid solution (in other words, the $\text{ZrO}_2 \rightarrow \alpha\text{-Zr-O}$ reaction) may render such a barrier layer ineffective. Other oxide layers such as chromia or yttria may have greater thermodynamic and kinetic stability with respect to dissolution to form the Zr-O solid solution phase. We are currently testing this hypothesis.

Others have observed porosity in oxidized FeCrAl [23, 24]. Various explanations have been proposed for the porosity, such as the volume change associated with the $\gamma\text{-}\alpha$ alumina

transformation, the incorporation of voids into rapidly growing alumina scale, and the coalescence of vacancies [23]. Further, hydroxides are thought to stabilize the porosity during steam exposure [23]. The last explanation for porosity (vacancy coalescence) is the result of the Kirkendall effect, referring to the counter flow of vacancies in response to net mass transport across an interface [30].

The porosity we observed in cross sectional STEM is confined to the original FeCrAl layer, the source of the Al, leading to disc pore morphology. This observation is not consistent with the γ - α alumina phase transformation or incorporation of voids into growing alumina leading to porosity. Alumina growth must be accompanied by a counter flow of vacancies across the Al_2O_3 -FeCrAl interface into the FeCrAl and this would explain the observed porosity. The Al atomic concentration in our FeCrAl films is 34%; complete depletion to form alumina with the greatest possible thickness would result in a porosity of ~33% by volume via the counter flow of vacancies into the FeCrAl. This simple estimate ignores Fe-Zr interdiffusion, the effect of Cr segregation (substantial at long exposure times, see for example Fig. 6F), the vacancy versus atomic specific volume, that the FeCrAl layer is not completely depleted of Al, and that some Al diffuses inward to the base Zr. All of these effects will act to reduce porosity via the Kirkendall effect and vacancy coalescence. Still, vacancy coalescence can result in significant porosity, not unlike what we observe here after long exposure times or in Reference 23. We also note porosity did not develop during exposure of the low Al/Cr-concentration sample (Zy2-4Al-700C-15h in Fig. 8F) where Fe_2O_3 oxide formed. This is another indication that alumina growth drives porosity.

XRD analysis of the FeCrAl-Zy2 autoclave test coupons indicates the formation of a NiFe_2O_4 spinel normal LWR coolant exposure conditions. Weight gain measurements indicate greater corrosion product formation for the coated specimens by approximately a factor of two at 20 days. This is likely due to the grain boundaries of the small grained coating layers facilitating precipitation of the observed spinel.

5. Summary

FeCrAl films of varying composition deposited on Zircaloy 2 have been investigated with respect to oxidation weight gain in 700 °C steam with the goal of impeding or eliminating rapid oxidation of the base metal. Most FeCrAl films studied here were ~1 μm thick. XRD analysis of as-grown FeCrAl with higher Al concentrations indicates a primitive cubic (Pm-3m) lattice structure that we attribute to the extended solid solution FeAl compound. Film compositions that promote alumina formation (Al concentration of 18 atomic percent or higher in this study) significantly reduced oxidation during high-temperature steam exposure, delayed the on-set of significant oxidation by 50-80 minutes, and reduced the heat generation rate by at least a factor of five. The growth of a near-surface alumina layer was quantified in AES depth profiles and demonstrated parabolic kinetics consistent with but greater than those observed by others in

high-temperature steam. Thick ($\sim 1\ \mu\text{m}$) FeCrAl films prevented oxidation of the underlying Zr up to 15 hours of steam exposure at $700\ ^\circ\text{C}$, while thin ($\sim 0.3\ \mu\text{m}$) FeCrAl films led to zirconia formation but at significantly reduced rates in $700\ ^\circ\text{C}$ steam.

High-temperature steam exposure and subsequent alumina formation resulted in a $\text{Pm-3m} \rightarrow \text{Im-3m}$ (BCC) lattice structure change in FeCrAl. The FeCrAl-Zr system exhibited a tendency for pore formation between the alumina layer and the underlying Zr substrate during $700\ ^\circ\text{C}$ steam exposure attributed to vacancy coalescence. Autoclave testing in a BWR environment ($288\ ^\circ\text{C}$ and $9.5\ \text{MPa}$) with normal water chemistry (2 ppm dissolved oxygen) up to 20 days indicates sufficient performance without loss of FeCrAl film integrity. The $900\ ^\circ\text{C}$ Fe-Zr eutectic resulted in complete film loss during $1100\ ^\circ\text{C}$ steam exposure of the FeCrAl-Zr system. Testing of the FeCrAl-YSZ system at 700 , 1100 , and $1250\ ^\circ\text{C}$ demonstrates the potential of YSZ and possibly zirconia (the thermodynamic stability of both may be a limitation) as a buffer layer to prevent the eutectic reaction. Post-exposure Fe and Al spinel structures, the former with some degree of inversion, were observed in the FeCrAl-YSZ system.

Implementation of a FeCrAl coating to promote oxidation resistance of Zircaloy cladding materials would require greater film thicknesses (at least tens of microns) than studied here. Additionally, a stable buffer layer may be required. We anticipate such film architectures would perform well with respect to oxidation in normal LWR environments and in high-temperature steam during off-normal transients.

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Table 1. Steam exposure sample identification matrix showing sputter growth conditions, exposure conditions, and microanalytical analysis techniques employed.

Sample	[Fe/Cr/Al]	x [nm]	P/V/I [W/V/A]	Exposure Environment			Analysis Techniques
				Phase	T [°C]	t [hr]	
Zy2-34Al-700C-15h	62/4/34	600	80/377/0.2	steam	700	15	STA, SEM, AES
Zy2-34Al-700C-10h	62/4/34	300	90/450/0.2	steam	700	10	STA, STEM/EDS, AES
Zy2-4Al-700C-15h	86/10/4	300	71/355/0.2	steam	700	15	STA, SEM, AES
Zy2-22Al-700C-15h	71/7/22	600	70/350/0.2	steam	700	15	STA, SEM, AES
Zy2-18Al-700C-15h	53/29/18	300	70/350/0.2	steam	700	15	STA, SEM/EDS, AES, XRD
Zy2-34Al-700C-3.7h	62/4/34	900	110/367/0.3	steam	700	3.7	STA, SEM/EDS, AES, XRD
Zy2-00Al-700C-15h	Uncoated	-----	-----	steam	700	15	STA
Zy2-34Al-000C-00h	62/4/34	900	110/367/0.3	-----	-----	-----	SEM/EDS, AES
Zy2-34Al-700C-2h				steam	700	2	STA, SEM/EDS, AES
Zy2-34Al-700C-0.5h						0.5	STA, SEM/EDS, AFM, AES
Zy2-34Al-000C-00h	62/4/34	570	108/355/0.3	-----	-----	-----	XRD
Zy2-00Al-700C-10h	Uncoated	-----	-----	steam	700	10	STA
Zy2-34Al-1100C-0.5h	62/4/34	1100	62/4/34	steam	1100	0.5	SEM
Zy2-34Al-000C-00h	62/4/34	1100	105/345/0.3	-----	-----	-----	AES, XRD
Zy2-34Al-700C-6h	62/4/34	1100	105/345/0.3	steam	700	6	STA, AES, XRD
Zy2-34Al-700C-5h						5	STA, AES
Zy2-34Al-700C-2h						2	STA, AES
Zy2-34Al-700C-0.5h						0.5	STA, AES, XRD
Zy2-34Al-700C-10h						10	STA, AES, XRD
Zy2-34Al-700C-15h						15	STA, AES
Zy2-34Al-700C-20h						20	STA, AES
YSZ-34Al-700C-3.5h	62/4/34	570	108/355/0.3	steam	700	3.5	SEM/EDS, AES
YSZ-34Al-000C-00h				-----	-----	-----	XRD
YSZ-34Al-1100C-2.5h				steam	1100	2.5	SEM/EDS, AES, XRD
YSZ-34Al-1250C-1h					1250	1	XRD
Si-34Al-000C-00h	62/4/34	1100	105/345/0.3		-----	-----	SEM

Table 2. Autoclave exposure sample identification matrix showing sputter growth conditions, exposure conditions, and microanalytical analysis techniques employed.

Sample	[Fe/Cr/Al]	x [nm]	P/V/I [W/V/A]	Exposure Environment			Analysis Techniques
				Phase	T [°C]	t [hr]	
Zy2-34Al-288C-240h	62/4/34	1100	105/334/0.3	BWR/ NWC	288	240	SEM, XRD
Zy2-34Al-288C-240h	62/4/34	1100	105/334/0.3	BWR/ NWC	288	240	
Zy2-00Al-288C-240h	Uncoated	1100	105/334/0.3	BWR/ NWC	288	240	SEM
Zy2-00Al-288C-240h	Uncoated	1100	105/334/0.3	BWR/ NWC	288	240	
Zy2-00Al-288C-240h	Uncoated	1100	105/334/0.3	BWR/ NWC	288	240	
Zy2-34Al-288C-480h	62/4/34	1100	105/334/0.3	BWR/ NWC	288	480	SEM, XRD
Zy2-34Al-288C-480h	62/4/34	1100	105/334/0.3	BWR/ NWC	288	480	
Zy2-00Al-288C-480h	Uncoated	1100	105/334/0.3	BWR/ NWC	288	480	SEM
Zy2-00Al-288C-480h	Uncoated	1100	105/334/0.3	BWR/ NWC	288	480	

Table 3. EDS composition analysis of YSZ-34Al-1100C-2.5h using 20 keV incident electrons.

Element	Composition [Atomic %]		
	Post-exposure Region 1	Post-exposure Region 2	As-grown
O	56.0	59.7	----
Al	6.7	26.6	62
Cr	2.1	1.3	4
Fe	34.1	7.8	34
Zr	1.1	4.6	----

Table 4. Parabolic rate constants K_p (steam [9] and dry O_2 [25]) and alumina layer thickness calculated for a 6 hour 700 °C exposure.

Reference	$K_p = D_o \exp(-E_a/kT)$		K_p (700 °C) [$g^2/cm^4/s$]	700 °C, 6 hour
	D_o [$g^2/cm^4/s$]	E_a [eV]		
[9]	8.02	2.79	2.8×10^{-14}	125
[25]	3.8×10^{-8}	1.46	1×10^{-15}	25
This work	AES		$2.3(0.1) \times 10^{-13}$	360
	Profilometer		$6(3) \times 10^{-14}$	180

Figure 1. Weight gain normalized to total sample surface area versus time during 700 °C steam exposure for FeCrAl samples with different compositions (A) and Fe/Cr/Al:62/4/34 (B). In both cases, the responses of uncoated Zy2 (Zy2-00Al-700C-15h and Zy2-00Al-700C-10h) are shown for comparison. This uncoated Zy2 response shows the expected pre-transition quasi-cubic kinetic behavior and eventual breakaway (linear) kinetics. The rollover behavior for Zy2-00Al-700C-15h and Zy2-4Al-700C-15h at long times (A) is due to sample consumption by the oxidation reaction. The uncertainty of the Zy2-34Al-700C-3.7h FeCrAl coated sample response indicated by the shaded band is discussed in the text.

Figure 2. ω - 2θ specular XRD scans of Fe/Cr/Al:62/4/34 films on YSZ substrates. FeCrAl at this atomic composition grows as primitive cubic (Pm-3m), with (100) reflection intensity that is forbidden for the BCC structure. The as-grown FeCrAl film is highly textured since intensity from the (110) reflection, the strongest in the Pm-3m powder pattern, is absent.

Figure 3. ω - 2θ specular XRD scan of as-grown Fe/Cr/Al:62/4/34 on Zy2. As with FeCrAl on YSZ, the FeCrAl film at this atomic composition grows as primitive cubic (Pm-3m). Unlike YSZ, however, the as-grown FeCrAl film is not textured and multiple reflections are observed from Zy2-34Al-000C-00h; all peaks can be indexed as Zr matrix or primitive cubic FeAl film reflections. Additional diffraction intensity indexed to α -alumina and a $\text{Fe}_2(\text{CrAl})$ (Fd-3m) intermetallic phase is observed from the Zy2-34Al-700C-10h sample exposed to 700 °C steam for 10 hours. The unindexed Zy2-34Al-700C-0.5h and Zy2-34Al-700C-10h diffraction intensity (for example, at $2\theta \sim 32^\circ$ in the Zy2-34Al-700C-0.5h pattern, at $2\theta \sim 41$ - 43° and 47° in Zy2-34Al-700C-10h) is likely due to intermetallic phase formation involving a combination of Fe, Al, Cr, and Zr.

Figure 4. 2θ glancing-angle XRD scans of the autoclave testing Zy2-34Al-288C-240h coupon compared to the ω - 2θ specular scan of as-grown Zy2-34Al-000C-00h. All reflections in Zy2-34Al-000C-00h are indexed to the Zr matrix or the FeAl primitive cubic (Pm-3m) structure. The autoclave coupon pattern is indexed to the Zr matrix, the Fe₃Al BCC (Im-3m), and the NiFe₂O₄ spinel. Glancing-angle diffraction geometry results in greater near-surface sensitivity and draws out the spinel diffraction intensity.

Figure 5. Weight gain per unit surface area for autoclave exposure samples for coated (red histogram bars) and uncoated (blue histogram bars). The 10- and 20-day exposures were performed in a Ni-based alloy autoclave, resulting in NiFe_2O_4 spinel precipitation, as discussed in the text. Each histogram bar represents a different sample. A total of four uncoated Zry2 specimens and five coated Zry2 specimens were exposed to BWR NWC autoclave environments (see Table 2).

Figure 6. AES depth profiles for Fe/Cr/Al:62/4/34 films: A) as-grown (Zy2-34Al-000C-00h); B-H) 700 °C steam exposure for sequentially longer times as indicated.

Figure 7. AES depth profiles for various FeCrAl compositions and film thicknesses: A and B) 700 °C, 10 hour steam (300 nm FeCrAl:62/4/34, Zy2-34Al-700C-10h); C and D) 700 °C, 15 hour steam (600 nm FeCrAl:62/4/34, Zy2-34Al-700C-15h); and E) 700 °C, 15 hour steam (300 nm FeCrAl:86/10/4, Zy2-4Al-700C-15h). Significant zirconia growth into the base metal is observed for these films. The AES depth profiles are extended to 8 μm in B and D showing the zirconia-ZrO solid solution interface.

Figure 8. Plan-view and cross-sectional SEM micrographs for FeCrAl films on Si (A) and Zy2 (B-F) as labeled. The cross section micrograph was used to calibrate film thickness growth rates and also exhibits columnar grain morphology. The as-grown plan view image (A) demonstrates a ~200 nm grain size. 700 °C steam exposure resulted in porosity in high Al/Cr composition films (C-E). A thick Fe-based oxide scale grew on the film with combined low Al/Cr concentration (F).

Figure 9. Cross-section STEM (A and B) and plan-view SEM (C) micrographs of Zy2-34Al-700C-10h, post-700 °C, 10 hour steam exposure. The cross sectional micrographs A and B show porosity between the alumina scale and the underlying zirconia that develops after prolonged steam exposure; B is a magnified region of the pore. The STEM micrographs were acquired at near-normal incident angle and the corresponding zirconia layer thickness is $\sim 1 \mu\text{m}$. The $\sim 1 \mu\text{m}$ pores are covered with alumina scale prone to cracking, as shown in C. The Pt layer was deposited as a protective layer for focused ion beam milling and to facilitate lift-out.

Figure 10. Plan-view SEM micrographs of the post-exposure autoclave coupons. The 10- (A) and 20-day (B) exposures were performed in a Ni-based alloy autoclave, resulting in NiFe_2O_4 spinel precipitation, as discussed in the text.

Figure 11. Plan-view SEM image of post-exposure YSZ-34Al-1100C-2.5h (1100 °C for 2.5 hours). SEM/EDS analysis was performed at two locations using a 20 keV incident electron beam and the compositions are listed in Table 3.

Figure 12. Time dependence of alumina oxide layer growth during 700 °C steam exposure obtained for AES depth profiles; open boxes (900 nm thick FeCrAl film, see Table 1), solid boxes (1100 nm thick FeCrAl film, see Table 1). Additional solid black plotting symbols correspond to profilometer measurements of a AES craters terminated at the alumina-Fe/Cr interface depth, as discussed in the text. The best-fit lines are proportional to the square root of the parabolic rate constants shown in the insets and listed in Table 4.

Weight gain normalized to total sample surface area versus time during 700 °C steam exposure for FeCrAl samples with different compositions (A) and Fe/Cr/Al:62/4/34 (B). In both cases, the responses of uncoated Zry2 (Zry2-13A and Zry2-19A) are shown for comparison. This uncoated Zry2 response shows the expected pre-transition quasi-cubic kinetic behavior and eventual breakaway (linear) kinetics.