

## Electrochemical Evaluations of Ferritic Steels (FeCrAl) for LWR Fuel Cladding to Enhance Accident Tolerance under Simulated LWR Conditions

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### 1. Introduction

After the March 2011 accident and plant black out caused by a tsunami at the Fukushima Daiichi nuclear power plant in Japan, in 2012 the US Department of Energy (DOE) initiated and organized an Accident Tolerant Fuel (ATF) Programs. The major requirement of ATF candidate materials to enhance the accident tolerance has been identified as to be; (1) Improved reaction kinetics with steam, (2) Lower or no hydrogen production, (3) Improved cladding and fuel properties, and (4) Enhanced retention of fission products. Currently, there are several ATF concepts being developed by the industry in cost sharing efforts with the US DOE, and among them, an iron-chrome-aluminum (FeCrAl) (e.g., APMT<sup>TM</sup>) cladding is chosen as an ATF candidate cladding material and being evaluated under various environmental test conditions [1-4].

The main characteristics of this FeCrAl alloy is its outstanding resistance to oxidation in high temperature water and steam, which was the weakness of the zirconium alloy in the Fukushima reactors. Other benefits that could make ferritic steels more attractive than the austenitic stainless steels in nuclear applications and specially as an ATF cladding include: (1) Ferritic materials have lower cost since they do not contain nickel (Ni), and generally contain lower chromium (Cr), (2) They do not contain nickel (Ni) or cobalt (Co) that could be become activated in commercial reactors, (3) They offer a lower coefficient of thermal expansion (CTE) that matches the CTE of pressure vessel ferritic alloys such as type A508, A516, or A533, and (4) Ferritic steels have higher thermal conductivity for heat transfer capabilities (Table 1) (Figure 1) [5].

The oxidation behavior of iron based alloys in steam was recently reviewed and updated comparing to the behavior of zirconium alloys [5, 6]. At 1200°C, the degradation of APMT was practically nil (no mass

change) after 8 h exposure at 1000°C while the degradation of Zircaloy-2 was complete for the same period of time. APMT offers extraordinary resistance to reaction with steam at temperatures higher than 1000°C because it allows first for the formation of a protective Cr<sub>2</sub>O<sub>3</sub> scale which subsequently allows for the formation of a continuous protective Al<sub>2</sub>O<sub>3</sub> scale between the metal and the Cr<sub>2</sub>O<sub>3</sub> scale. It is this Al<sub>2</sub>O<sub>3</sub> scale what protects the alloy against further oxidation in steam. Pint et al. also reported that the content of Cr is important and that, in the absence of Al, at least a 25% of Cr may be required in the iron alloy to offer protection against steam [6].

Table 1: Physical properties of ferritic and austenitic steels [5]

Material	CTE (0-538°C) $\mu\text{m/m}^\circ\text{C}$	Thermal Conductivity at 100°C (W/m.K)
Zircaloy-2	8.32 & 15.7 (orientation dependent)	13.8
Ferritic type 430 (16% Cr)	11.4	23.9
Austenitic type 304L (18% Cr)	18.4	16.2



Figure 1: Desirable characteristics of ferritic steels for ATF cladding [5]

However, even though austenitic stainless steel were used for fuel rod cladding in the first PWRs, FeCrAl alloys have never been used in light water reactors and their corrosion and electrochemical behavior in  $\sim 300^\circ\text{C}$  water thus needs to be characterized. It is well known that the electrochemical corrosion behavior of the materials depends on the water chemistry conditions, the oxide surface nature, such as oxide thickness, composition, conductivity, microstructure, etc. Also, a change in electrocatalytic nature of the surface associated with the chemical compositions of the oxide layers can play a significant role in the free corrosion potential behavior of the materials.

Thus, the high temperature electrochemical behavior of FeCrAl alloy for ATF cladding material was evaluated under simulated LWR conditions to be compared with the well-known behavior of traditional reactor materials (e.g., Zr alloys). Table 2 lists the test specimens and their chemical compositions.

Table 2: Nominal composition of test specimens

	Alloy	Nominal Composition
A	Zirc-2 UNS R60802	Zr + 1.2-1.7 Sn + 0.07-0.2 Fe + 0.05-0.15 Cr + 0.03-0.08 Ni
B	Ferritic steel T91 K90901	Fe + 9 Cr + 1 Mo + 0.2 V
C	Ferritic steel HT9 S42100	Fe + 12 Cr + 1 Mo + 0.5 Ni + 0.5 W + 0.3 V
D	Nano ferritic alloys NFA	e.g. 14YWT; Fe + 14 Cr + 0.4 Ti + 3 W + 0.25 $\text{Y}_2\text{O}_3$
E	MA956 or UNS S67956	Fe + 18.5-21.5 Cr + 3.75-5.75 Al + 0.2-0.6 Ti + 0.3-0.7 $\text{Y}_2\text{O}_3$
G	APMT	Fe + 22 Cr + 5 Al + 3 Mo
H	High Cr Ebrite S44627	Fe + 25-27.5 Cr + 1 Mo + 0.17 (Ni + Cu)
J	Alloy 33 - UNS R20033	33 Cr + 32 Fe + 31 Ni + 1.6 Mo + 0.6Cu + 0.4 N

## 2.Experimental Results and Discussions

Figure 2 shows the corrosion potential behavior of 304 SS, Alloy X-750, Pt and several advanced steels such as APMT in  $288^\circ\text{C}$  water under various water chemistry conditions. Under oxidizing water chemistry conditions (0.6 ppm and 1 ppm  $\text{O}_2$ ) and reducing water chemistry conditions (0.1 and 0.15 ppm  $\text{H}_2$ ), the corrosion potential of advanced steels (APMT, Alloy 33, and NFA) were very similar to that of the well-known materials such as 304SS and X-750. The corrosion potential of Zircaloy-2 was always lower than that of other electrodes due to the formation of insulating oxide,  $\text{ZrO}_2$  that limited the  $\text{O}_2$  reduction kinetics. Based on the ECP data, it is clear that the redox kinetics on ferritic advanced steel alloys behaves similarly to that of 304SS or X-750 in high temperature water.

The enhanced growth of Zr oxides has been observed in BWR on areas of Zircaloy 2 cladding that are

close/adjacent to other metals such as nickel base alloys and stainless steels. This anomalous growth in the oxide of the Zircaloy 2 is called “shadow corrosion” since the enhanced corrosion shape on the zirconium alloy component resembles the imprint on the other stainless steel or nickel alloy metallic component [7]. Two hypothesis have been used to explain this phenomenon; (1) galvanic corrosion and (2) local radiolysis; however, there are evidences that these two hypotheses may not explain all the occurrences of shadow corrosion

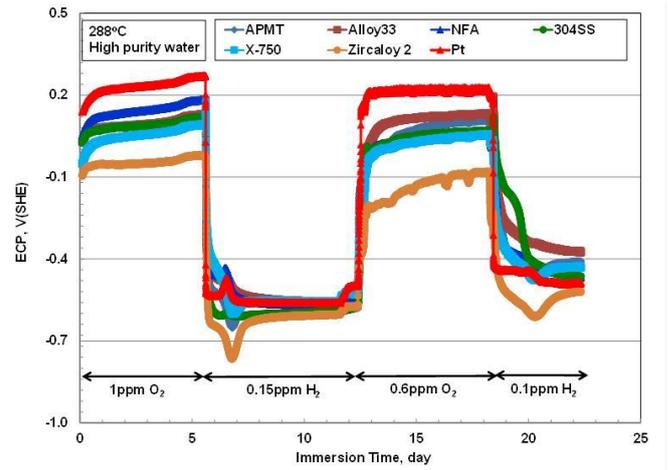


Figure 2: ECP behavior of various materials in  $288^\circ\text{C}$  water containing different concentration of  $\text{H}_2$  and  $\text{O}_2$ .

In the laboratory autoclaves, the plant irradiation behavior has been simulated using a ultra violet (UV) illumination [7]. The ECP behavior of Zircaloy-2, X-750 and ferritic alloys was measured in  $288^\circ\text{C}$  water containing 1 ppm  $\text{O}_2$  with and without UV illumination, as shown in Figure 3. The presence of UV light decreased the corrosion potential of Zircaloy-2, but increased the corrosion potential of X-750 in high temperature water. This change in the corrosion potential in the presence of UV light can be explained by the photo excitation of  $n$ -type  $\text{ZrO}_2$  formed on Zircaloy-2 and  $p$ -type  $\text{NiO}$  on X-750. Also, the ECP of both alloys returned to the previous value when the UV light turned off, indicating no significant residual effect of UV light on the oxide properties of  $\text{ZrO}_2$  and  $\text{NiO}$ .

Figure 3 also indicates that X-750 and ferritic alloys behave in a similar way regarding the shift in their ECPs under both water chemistry conditions with and without UV. This means that a Zircaloy-2 component coupled to a X-750 spacer may suffer shadow corrosion in presence of oxidants in the reactor because their corrosion potential grow apart from each other when irradiation is present. However, the ECP response under a UV irradiation suggests that a APMT cladding would not

adopt a different corrosion potential of a X-750 spacer and therefore would not suffer shadow corrosion in the reactor core. Thus, if a FeCrAl steel is used for the LWR cladding, shadow corrosion may not occur since under irradiation the ECP of FeCrAl and nickel alloys such as X-750 would be the same.

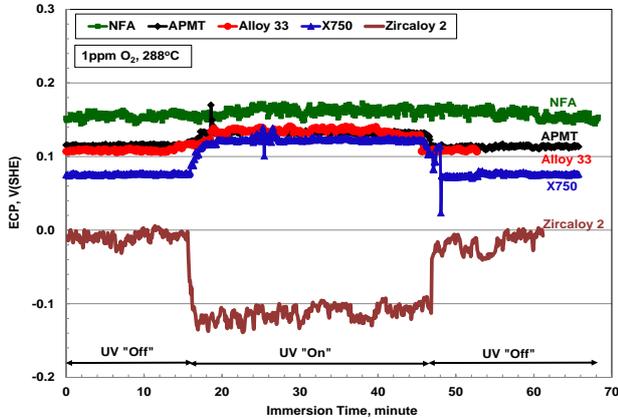


Figure 3: Effect of UV illumination on the ECP of Zircaloy 2, X-750 and ferritic steels in 288°C water containing 1 ppm O<sub>2</sub>.

Specimen of 20% cold worked Alloy APMT was tested for SCC resistance in high temperature water [5]. The effect of frequency on crack growth rate and crack arrest is shown in Figure 4. APMT shows a similar behavior as other ferritic steels, that is, SCC crack propagation is not sustainable under non cyclic loading conditions, even for high applied stress intensity values of 40 ksi√in.

All of the ferritic alloys being evaluated for SCC response in this program have excellent resistance to stress corrosion cracking, even under quite aggressive conditions of elevated oxidants (2 ppm dissolved O<sub>2</sub>) and 30 ppb sulfate or chloride (well above that allowed by the BWR water chemistry guidelines). All crack propagation under cyclic loading condition can be considered fatigue cracking. Only under constant load conditions (R=1) the crack propagation may be recognized as environmentally assisted cracking or stress corrosion cracking (SCC). Current results show that ferritic steels containing chromium are extremely resistant to cracking in high temperature water.

During its lifetime performance under normal operation conditions it is essential that the cladding does not breach releasing fission products from the fuel into the water. That is, similarly to the actual zirconium based alloys, the candidate replacement alloys should not corrode excessively in water at ~300°C nor suffer environmentally assisted cracking under similar conditions. The life of a fuel bundle in a commercial

reactor is generally less than 10 years, that is, under normal operation conditions the cladding should be able to maintain hermetic integrity for this period of time [5].

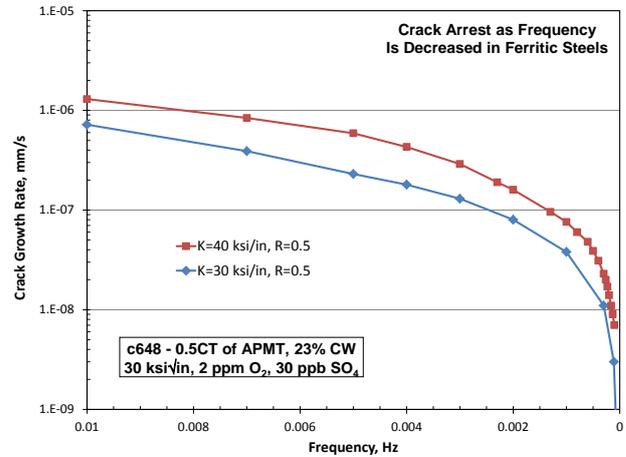


Figure 4: Crack growth rate vs. frequency for specimen c648 of a 23% cold worked APMT alloy in 288 °C water containing 2 ppm dissolved oxygen and 30 ppb sulfate as H<sub>2</sub>SO<sub>4</sub> showing that crack arrest occurs as frequency is decreased

Figure 5 shows the mass change rate for two coupons each of Zircaloy 2 (the current baseline material for cladding in commercial light water reactors) and various ferritic steels (MA956, APMT, Ebrite and Alloy 33). It is clear that all the ferritic steels had a mass gain rate lower than that for Zircaloy-2. The data for one year exposure shows that the mass gain rate for APMT was approximately one order of magnitude lower than for Zircaloy-2.

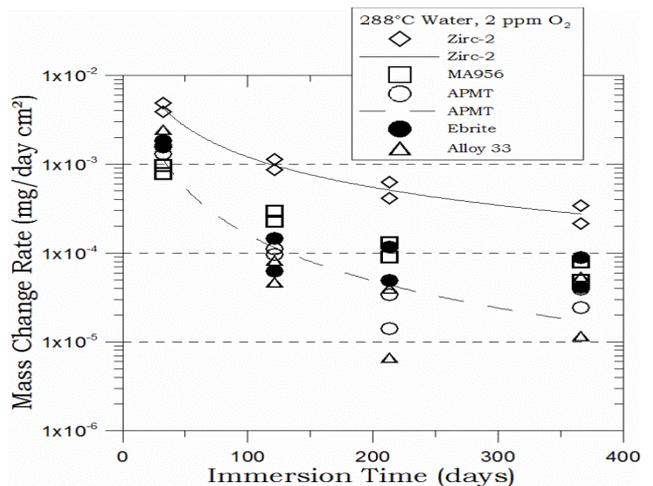


Figure 5. Mass change per unit area and unit time for Zirc-2, MA956, APMT, Ebrite and Alloy 33 coupons exposed to pure water + 2 ppm O<sub>2</sub> at 288°C for a total time of 366 days.

## Summary

It is clearly evident that ferritic steels (e.g., APMT alloys) are highly resistant to corrosion and environmental cracking under normal operation conditions. That is, the replacement of a zirconium alloy using a ferritic material containing chromium and aluminum appears to be the most near term implementation for accident tolerant fuels.

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## REFERENCES

- [1] R. E. Stachowski, R. B. Rebak, W. P. Gassmann, J. Williams, "Progress of GE Development of Accident Tolerant Fuel FeCrAl Cladding," Top Fuel 2016, Boise Idaho, September 2016
- [2] K. A. Terrani, B. A. Pint, Y.-J. Kim, K. A. Unocic, Y. Yang, C. M. Silva, H. M. Meyer III, and R.B. Rebak, "Uniform corrosion of FeCrAl alloys in LWR coolant environments," *J. of Nuclear Materials*, 479 (2016), pp. 36-47.
- [3] R. B. Rebak, M. Larsen, and Y.-J. Kim, "Characterization of Oxides Formed on Iron-Chromium-Aluminum alloy in Simulated Light Water Reactor Environments," accepted for publication in *Corrosion Reviews* (2017).
- [4] R.B. Raul, T.B. Jurewicz, & Y-J Kim, "Oxidation Resistance of FeCrAl in Simulated BWR and PWR Water Chemistries", Top Fuel 2017, Jeju, Korea, September 2017.
- [5] R.B. Rebak, P.L. Andresen, Y-J Kim, E. Dolley, "Characterization of Advanced Steels as Accident Tolerant Fuel Cladding for Light Water Reactors", IAEA ATF Meeting, ORNL, 2014.
- [6] B.A. Nt, M.P.. Brady, J.R. Kaiser, T. Cheng, K.A. Terrani, "High Temperature Oxidation of Fuel Cladding Candidate Materials in Steam-Hydrogen Environments," Proceedings of the 8th International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, France, May 2012, Paper #89.
- [7] Y. -J. Kim, R. B. Rebak, Y.-P. Lin, D. Lutz, D. Crawford, A. Kucuk, and B. Cheng, "Photoelectrochemical Investigation of Radiation-Enhanced Shadow Corrosion Phenomenon," *Journal of ASTM International*, Vol. 7, No. 7, Paper ID JA1102952 (2010)
- [8] P.L.Andresen, R.B. Rebak, E.J. Dolley, "SCC Growth Rate of Irradiated and Unirradiated High Cr Ferritic Steels," presented at Fontevraud 8, Contribution of Materials Investigations and Operating Experience to LWRs' Safety, Performance and Reliability, 15-18 September 2014, Avignon, France