MP MATERIALS PERFORMANCE
CORROSION
INNOVATION OF THE YEAR AWARDS

2019 Award Nomination

Title of Innovation: FeCrAl Accident Tolerant Fuel Cladding

Nominee(s)

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Category: Materials Design

Dates of Innovation Development:
FeCrAl (C26M/IronClad) Accident Tolerant Fuel Cladding: laboratory development 2012-2016; licensing and scale-up 2016-present

Web site: www.ornl.gov; www.ge.com;

Summary Description: The nuclear incident that occurred at the Fukushima Daiichi Nuclear Power Plant in 2011 showed the world the implications of using Zr-based materials, which rapidly and exothermically oxidize in steam environments, in the nuclear core during accident scenarios. Since the Fukushima Daiichi incident, a range of material systems have been developed that will not oxidize in the same manner as the Zr-based materials resulting in enhanced accident tolerance of the global nuclear reactor fleet. Iron-chromium-aluminum (FeCrAl) alloys in initial screening experiments showed potential as a material system to replace Zr-based alloys but typical commercialized FeCrAl alloys studied at the time (2012) did not have other properties that were acceptable for use in a nuclear fuel environment. The culmination of a multi-year, multi-faceted research, development, and deployment (RD&D) project has led to the production of a FeCrAl cladding deemed acceptable for pilot testing as an accident tolerant fuel (ATF) cladding. The basis of the RD&D effort was the optimization of the Cr and Al and solute additions to maintain high temperature oxidation resistance without significant detriment to other performance factors such strength, ductility, radiation tolerance, and fabricability, to name a few. The result of these efforts produced the nuclear-grade FeCrAl ATF cladding, IronClad, which is now available in pre-commercial product forms.

Full Description:

1. What is the innovation?

Conventional nuclear fuel cores use Zr-based alloys such as Zircaloy 2, Zircaloy 4, ZIRLO, and M5 as cladding around the nuclear fuel. The role of the nuclear fuel cladding is to contain the radionuclides of the fuel during both normal operation and during design basis accident scenarios. The choice of Zr-based alloys for this role is primarily due to the neutronic transparency of Zr, which increases the efficiency of the core, and the acceptable performance under normal operation through decades long alloy optimization efforts by the nuclear industry. The issue with using Zr-based alloys as nuclear fuel cladding is the limited safety margins, e.g. time to onset of severe core degradation, under accident scenarios. The reason for such limited time of core performance in accident scenarios is the rate of oxidation under high temperature (>1000°C) steam environments that also leads to the production of hydrogen and further energy into the system. This effect was dramatically put on display during the 2011 Fukushima Daiichi Nuclear Power Plant incident.

A fundamental engineering response to reduce the severity of future Fukushima-like accidents is to increase the oxidation resistance of the nuclear fuel cladding. At first take, coatings are the lowest-cost & fastest to market solution to increase the oxidation resistance of the cladding but there remain uncertainties in overall performance and robustness for the coated Zr-based cladding technologies. One solution that has been under development since 2012 is the use of a monolithic cladding composed of an Iron-Chromium-Aluminum (FeCrAl) alloy. FeCrAl alloys, such as APMT, can demonstrate significantly reduced oxidation resistance compared to Zr-based alloys as shown in Figure 1. The increased oxidation resistance in FeCrAl alloys is the result of the alloys ability to form aluminum oxide (alumina, Al_2O_3) in high temperature steam environments.

The advantage of the oxidation resistance demonstrated in Figure 1 for FeCrAl alloys has been demonstrated through modeling efforts to increase the coping time (e.g. the time the core remains recoverable under an accident scenario) [1,2]. Despite the demonstrated benefit of using FeCrAl alloys in nuclear fuel applications, the commercially available alloys at the time of the Fukushima Daiichi accident were not considered for, and thus not optimized for, nuclear fuel cladding applications due to the expected fuel efficiency reduction associated with increased neutron absorptions.

Fuel cladding performance characteristics are multi-dimensional and include consideration of neutronic performance, mechanical performance, radiation tolerance, and fabricability to name a few. Preliminary investigations found that a balance of Cr and Al, as well as minor solute additions are needed to begin meeting the stringent demands for FeCrAl use in a nuclear core. For example, FeCrAl alloys exhibit a low temperature miscibility gap (<500°C) that can lead to deleterious precipitation and material embrittlement under thermal aging and irradiation [3]. Nuclear fuel cladding operates within this miscibility gap (290-330°C). The severity of the precipitation is reduced with reduced Cr and increased Al contents in the FeCrAl alloy. This balance is in direct competition with the high-temperature steam oxidation resistance where low-Cr variants may not remain protective in accident scenarios depending on the Al content, Figure 2. Similar compositional dependencies exist for many other performance factors including thin-wall tube fabrication, mechanical performance – including fracture toughness, and welding [4].

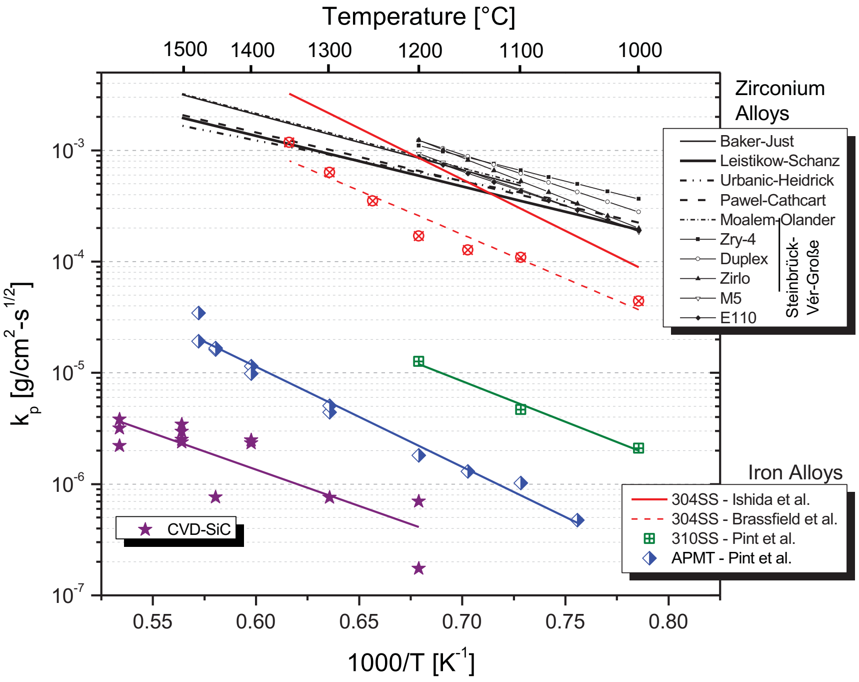

Figure 1: Arrhenius plot of the parabolic weight-gain rate constants for Zr-based and Fe-based alloys in steam. APMT is a representative FeCrAl alloy for comparison to the Zr-based alloys. Figure from Ref. [5].

The innovation lies in optimizing *both* the composition and microstructure for performance in a nuclear power plant under *both* normal operation and accident scenarios. Recently, Oak Ridge National Laboratory in collaboration with General Electric's Global Research Center and Global Nuclear Fuel has completed an extensive research, development, and deployment (RD&D) program to develop a new FeCrAl alloy, known internally at ORNL as C26M and commercially as IronClad, for nuclear fuel applications. IronClad has a balanced level of alloying additions and optimized processing route to commercially produce cladding deemed "accident tolerant" while still satisfying the normal operation demands of nuclear fuel cladding. On February 13th, 2018 the C26M alloy, produced using commercial processes in conjunction with Global Nuclear

Fuel (GNF), was inserted into Plant Hatch, Unit 1 as a lead test assembly. This insertion signals the ushering of a new era of global nuclear reactor operation using accident tolerant fuel assemblies. This insertion of IronClad represents the first novel fuel-clad concept inserted into a commercial reactor core in over 30 years.

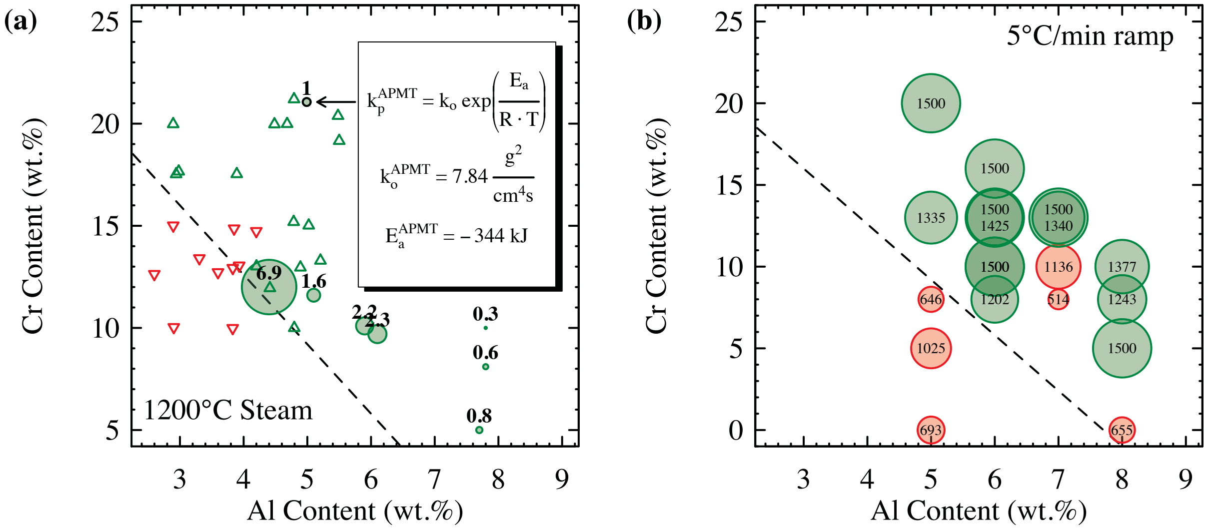

Figure 2: Effect of Cr and Al alloy content on steam oxidation resistance at 1200°C in FeCrAl alloys. (a) green, up-triangle symbols showing compositions which form a protective alumina scale and red, down-triangle symbols are those that are not protective [6], dashed line is arbitrary boundary separating the two regimes. Where kinetic data is available [7] circles are scaled with the scaling factor (S) presented to the Kanthal APMT parabolic oxidation rate as shown in inset, $\boxed{k_p^{Cr,Al} = S \cdot k_p^{APMT:1200°C}}$. (b) maximum use temperature determined via "ramp" testing, green circles are alloys with maximum use above 1200°C [8]. Figure reproduced from [4].

2. How does the innovation work?

The development of the IronClad alloy was aided by computational thermodynamic calculations to guide alloy design. Four key experimental findings underpin the successful development of the IronClad alloy:

1. *Oxidation:* As demonstrated in Figure 2, protective alumina surfaces can be formed in elevated oxidizing environments on FeCrAl alloys only when the weight percent of Al and Cr are between 3-5 and >12, respectively. Cr, with the addition of Y, helps to establish and stabilize the alumina surface under oxidizing environments. The compositional regime promotes a fully ferritic microstructure with no possibilities for intermetallic formation. The composition of IronClad exists within the compositional range where protective alumina formation is promoted.

2. *Corrosion:* The unique combination of Cr and Al concentration also means that at lower temperatures (~300°C) the FeCrAl alloy is a chromia former and not an alumina former. This promotes protective chormia formation in water chemistry environments typical of light water reactors and prevents long-term aqueous-based corrosion of the cladding [9]. The neutronics of the IronClad means that thinner claddings are needed. The low corrosion rate due to the chromia formation means that structural integrity will remain on the thinner FeCrAl cladding under normal operation.

3. *Radiation Tolerance:* Good radiation tolerance was achieved by reducing the Cr content to 12 wt.% Cr and increasing the Al content above 5 wt.% Al [10]. Fabrication steps were taken to also promote a fine grain structure which enhances the radiation tolerance of the alloy. Composition and microstructure control primarily limits phase instabilities under radiation reducing the possibility for radiation-induced embrittlement.

4. *Fabricability:* The composition control for IronClad also enables the ability for the material to be warm drawn and pilgered readily into final form factors for commercial deployment. Elevated Cr or Al contents would lead to cracking under drawing or pilgering as well as during welding [11,12].

3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

During the beyond design basis accident (BDBA) at the Fukushima Daiichi nuclear power plant in March 2011, the Zr alloy fuel cladding oxidized rapidly in steam forming hydrogen gas and generating more heat from the oxidation reaction than the decay heat from the reactor fuel. The hydrogen reaction product eventually led to the explosions at the plant and exacerbated the severity of the event. In response, a research program was initiated at ORNL to develop more accident tolerant fuel cladding materials with the metric of having a reaction rate ≥100× lower than Zr at 1200°C. A broad-based survey identified FeCrAl alloys with Y additions as attractive candidates.

FeCrAl alloys with Y additions have been investigated since the 1950's because of their ability to form a protective alumina scale at high temperature and are used in a variety of high temperature applications including heating elements (e.g. Kanthal) and catalyst supports. As described above, conventional commercial FeCrAl alloys did not have the correct combination of Cr and Al for this application. They typically contain either 20-21 wt.% Cr and ~5 wt.% Al for the highest temperature applications or leaner compositions have 10-14 wt.% Cr and 2-4 wt.% Al for applications that require better mechanical properties and ease of fabrication. The research effort found that the leaner compositions could not form alumina in steam at 1200°C. However, for radiation resistance, low Cr contents were desirable. The alloy development effort identified that above 6 wt.% Al the alloy was too brittle to be fabricated into thin tubing. Thus, the current composition of 12 wt.% Cr and 6 wt.% Al was unlike any previous FeCrAl composition and found to possess the best oxidation resistance and, remarkably, can form protective alumina up to 1500°C during heating in steam at 10°C/min (to simulate an accident scenario). The alloy melts at ~1520°C so its oxidation resistance in steam is outstanding. The composition is also corrosion resistant in the normal operating conditions of a light water reactor of pressurized water at ~300°C. Unlike austenitic steels, ferritic steels like IronClad are not susceptible to stress corrosion cracking and have been tested in autoclaves for more than 1 year to prove their durability during normal operation.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

The IronClad concept and family of pre-cursor alloys have been extensively tested in both single effects and integral tests within laboratory and simulated field trails – see reference for detailed discussions [4]. Performance factors such as mechanical strength, radiation tolerance, and fabrication have all been tested and shown success. Ramp testing in 1 bar of steam which simulates accident scenarios of nuclear reactors have demonstrated no significant mass gain of the IronClad (C26M) product, Figure 3**Error! Reference source not found.**. The mass change data in Figure 3 indicates protective alumina formation with reduced kinetics compared to the currently deployed Zr-based alloys. Similarly, autoclave testing under conditions relevant to normal operation of light water reactors has shown limited hydrothermal corrosion and no stress corrosion cracking [13,14].

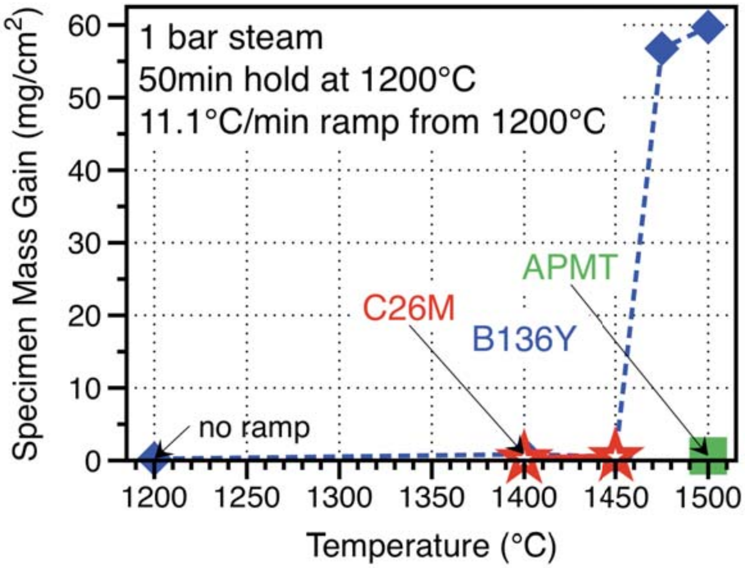

Figure 3: Ramp testing simulating the oxidizing environment during accident scenarios of nuclear power plants for IronClad (C26M).

To complement the separate effects accident tests, a large scale integral test with >60 m of IronClad fuel cladding rods internally heated in flowing steam was performed at Karlsruhe Institute of Technology's QUENCH facility [15] (Karlsruhe, Germany). The IronClad test parameters were initially conducted to mimic multiple previous tests on Zr-based cladding and were subsequently extended into accident regimes far more severe than the previous Zr-based tests. In a direct comparison to Zr-based cladding, the IronClad material experienced almost no discernable oxidation since the autocatalytic temperature excursion due to rapid oxidation of susceptible Zr-based alloys was absent. Even after extending the test into power and time regimes well-beyond what is possible with Zr-based cladding, the IronClad material experienced limited oxidation and produced significantly less hydrogen gas.

Figure 4: Assembly of QUENCH-19 test with IronClad rods at Karlsruhe Institute of Technology. The test assembly was heated using electrical heaters inside the cladding to simulate heat from radioactive decay while being subjected to high temperature flowing steam. The ~3h test reached a temperature of ~1400°C that is 500°C lower than what is experienced at much shorter time with oxidation-susceptible Zr-based cladding and produced at least an order of magnitude lower hydrogen gas.

Finally, the pre-commercial IronClad products have been and are being tested in both simulated environments in materials test reactors and within commercially operating nuclear power reactors. The IFA-796 experiment using UO_2 fueled IronClad assemblies within the Halden Boiling Water Reactor (Halden, Norway) were neturon irradiated up to a peak burnup of 4.5 MWd/kg UO_2. The fueled assemblies were irradiated under typical pressurized water reactor (PWR) conditions with 4.6 ppm Li with boron additions aimed at maintaining a pH_{300} of ~7.3. Inlet and outlet temperatures of the experimental rig was maintained near 300°C. Visual inspection shown in Figure 5 and in-situ data collection of the assemblies shows successful operation of the pre-commercial IronClad products within this simulated materials test reactor experiment. Building on this successful testing, additional product was deployed into Southern Nuclear's Plant Hatch, Unit 1 during the Cycle 29 refueling outage. Four Lead Test Assemblies (LTAs) of the conventional GNF2 design were used to house IronClad product in standard fuel rod positions. The overarching objectives of the IronClad containing LTAs are (1) confirm fundamental Fuel-Cladding-Reactor environment compatibility, (2) confirm cladding creep characteristics in commercial reactor environments, and (3) enable the specimens to be used for subsequent tests. Field testing continues on the LTAs with roll-out of additional testing in other commercially operating nuclear power plants planned.

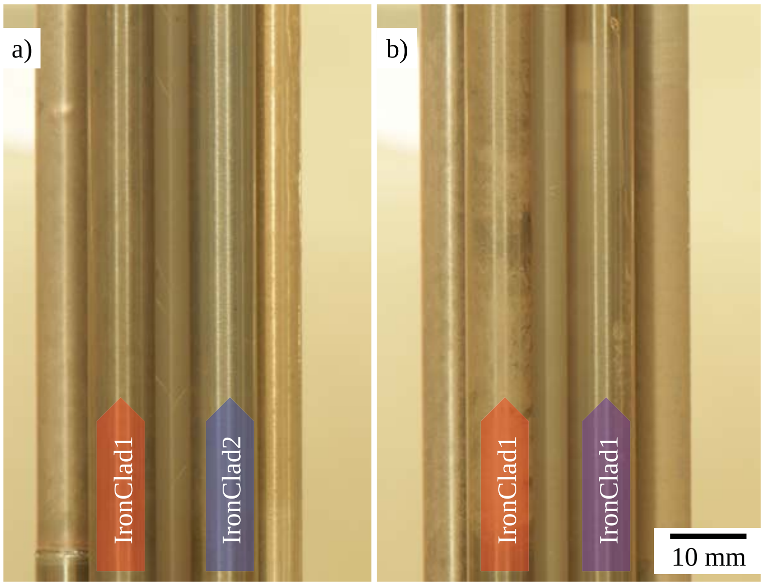

Figure 5: Fueled rodlets for a full length rodlet (red label) and segmented rods (blue and purple labels) for IronClad after one cycle (1.4 MWd/kgUO2) in the IFA-796 experiment.

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

IronClad can be retrofitted into otherwise normal production of fuel assemblies or customized for a given application. The product has been designed to have no significant impacts on the performance of a nuclear reactor while simultaneously increasing the inherent safety. The increased safety of IronClad has additional impacts on reducing operating costs by possibly reducing the nuclear exclusion zone.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

The IronClad concept was deployed in the first commercial field-test in February 2018 with praise from the Nuclear Industry including the Department of Energy and is now available as a pre-commercial product for additional trials and field tests. Commercial scale pre-cursor heats (>400 lbs) have been procured and produced into various fuel cladding final form factors using commercial vendors and processes. Figure 6 shows a mock up the IronClad concept. The IronClad product is currently scheduled for continued deployment in commercially operating nuclear reactors as a pilot program for full-scale deployment within the global nuclear fleet.

Figure 6: Mock-up of IronClad in a commercial fuel assembly.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

Patents were not filed by ORNL with the expectation that open-source development would fuel innovation within the FeCrAl alloy class and shorten the time from concept to commercialization similar to the experience for Grade 91 steel, which was jointly developed by ORNL in the early 1980's and now is used worldwide.

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