



Invited Article

Improving Accident Tolerance of Nuclear Fuel with Coated Mo-alloy Cladding

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ABSTRACT

In severe loss of coolant accidents (LOCA), similar to those experienced at Fukushima Daiichi and Three Mile Island Unit 1, the zirconium alloy fuel cladding materials are rapidly heated due to nuclear decay heating and rapid exothermic oxidation of zirconium with steam. This heating causes the cladding to rapidly react with steam, lose strength, burst or collapse, and generate large quantities of hydrogen gas. Although maintaining core cooling remains the highest priority in accident management, an accident tolerant fuel (ATF) design may extend coping and recovery time for operators to restore emergency power, and cooling, and achieve safe shutdown. An ATF is required to possess high resistance to steam oxidation to reduce hydrogen generation and sufficient mechanical strength to maintain fuel rod integrity and core coolability. The initiative undertaken by Electric Power Research Institute (EPRI) is to demonstrate the feasibility of developing an ATF cladding with capability to maintain its integrity in 1,200–1,500°C steam for at least 24 hours. This ATF cladding utilizes thin-walled Mo-alloys coated with oxidation-resistant surface layers. The basic design consists of a thin-walled Mo alloy structural tube with a metallurgically bonded, oxidation-resistant outer layer. Two options are being investigated: a commercially available iron, chromium, and aluminum alloy with excellent high temperature oxidation resistance, and a Zr alloy with demonstrated corrosion resistance. As these composite claddings will incorporate either no Zr, or thin Zr outer layers, hydrogen generation under severe LOCA conditions will be greatly reduced. Key technical challenges and uncertainties specific to Mo alloy fuel cladding include: economic core design, industrial scale fabricability, radiation embrittlement, and corrosion and oxidation resistance during normal operation, transients, and severe accidents. Progress in each aspect has been made and key results are discussed in this document. In addition to assisting plants in meeting Light Water Reactor (LWR) challenges, accident-tolerant Mo-based cladding technologies are expected to be applicable for use in high-temperature helium and molten salt reactor designs, as well as nonnuclear high temperature applications.

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1. Introduction

The behavior of nuclear fuel rods in a station blackout (SBO) accident has been analyzed using MAAP [1] and MELCOR [2] codes. The results indicate that extending the availability of a battery-assisted passive cooling system to remove the nuclear decay heat is of utmost importance in delaying fuel temperature rises and core damage. Current generation plants are designed to have 4–24 hour passive cooling capacity, whereas the Generation III+ plants under construction extends that capacity to 72 hours.

After the loss of battery-assisted passive cooling, water in the reactor core will absorb the decay heat and vaporize to steam. As the steam temperature rises, oxidation of the Zr-alloy cladding will accelerate which releases hydrogen as well as significant chemical heat due to the large enthalpy of formation of ZrO_2 . Rapid oxidation of Zr-alloy fuel cladding will start at 700–1,000°C under high steam pressure. Furthermore, fuel rod collapse and dislocation may occur at temperatures exceeding ~900°C, as Zr-alloys lose substantially its mechanical strength at >850°C. If the reactor core loses its pressure, such as in a design base loss of coolant accidents (LOCA) due to a pipe breakage, fuel rod ballooning and burst may occur. Dispersion of volatile fission products will occur while the fuel pellets are largely exposed. Fuel pellets will melt at ~2,500°C.

To recover a plant from entering a station blackout accident requires resupply of coolant into the core, either by reactivating the high pressure cooling system if AC power is available and the system is functional, or injecting coolant at low pressure after the core is depressurized. The time available for operators to recover from a severe accident is short because of rapid oxidation of the Zr-alloy cladding and the resultant hydrogen release. Evaluation of alternate fuel rod designs to enhance tolerance to a severe accident was started following the Fukushima Daiichi accident in 2011, and the focus has been mainly in fuel designs for current light water reactors.

A scoping analysis using the MAAP code was performed to evaluate how an ideal accident tolerant cladding (ATF) with total resistance to steam reaction until melting at ~2,500°C would enhance fuel resistance to damage in a severe accident. The results reported in [1] suggest that a gain of ~28 hours and 5 hours may be achieved for typical Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR), respectively, on top of the estimated 11 hours for a plant with availability of passive cooling for 72 hours. Slightly less gains may be achieved for plants with passive cooling lasting for 24 hours. In realistic cases, gains of ~5 hours and ~20 hours may be achieved for PWRs, if the fuel rod is resistant to steam attacks at 1,200°C and 1,500°C, respectively.

The United States (US) Department of Energy (DOE) launched a multi-year research and development (R&D) program with funding to the national laboratories and nuclear fuel vendors to develop enhanced accident tolerant fuel (ATF) in 2012 [2]. Various international programs have also been launched over the past 3 years [4]. Candidate new cladding materials have included: coated Zr-alloy, SiC–SiC_f composite, Al-containing stainless steel, and refractory metal (primarily molybdenum alloy).

EPRI initiated an independent research project in 2012 with conceptual designs of coated molybdenum alloy as an ATF cladding to achieve accident resistance to a temperature range of 1,200–1,500°C [3,4]. The EPRI task is to study the feasibility of fabrication of coated Mo-alloy cladding and perform tests to demonstrate its capability to meet the stringent requirements for normal operation and maintaining fuel rod geometry, and oxidation resistance at 1,200–1,500°C in a severe accident.

1.1. Coated Mo-Alloy design basis

The design concept for an accident tolerant fuel is to develop an all metallic fuel cladding to replace the current Zr-alloy cladding. Zr-alloys behave like a super plastic as it loses all strength due to rapid self-diffusion and crystallographic phase transition at ~850°C, therefore, coating on Zr-alloys will not meet our ATF design concept. Ceramic materials are excluded from consideration for current fuel design configurations primarily due to their absence of ductility which will not likely meet fuel thermal–mechanical performance and fuel reliability requirements once a ceramic cladding comes in contact with UO_2 fuel pellets.

Metals and alloys with neutronic, corrosion, and oxidation resistance and mechanical properties to meet fuel design criteria are very limited. There is no engineering metal or alloy available to match the low thermal absorption property of zirconium. Stainless steel (Fe–Cr–Ni) was used as the first generation fuel rod cladding; however, iron-based alloys will not likely meet the strength requirements at temperatures exceeding 1,000°C. Mo-alloy has a thermal neutron absorption cross-section similar to that of steels, and it has a melting temperature of 2,623°C with known high-strength properties at elevated temperatures, e.g., 60–80 MPa (~10 ksi) at 1,500°C. The high melting temperature and high strength of Mo alloys also have been associated with challenges in fabrication and engineering applications has been limited. Mo-alloys were considered for high temperature space reactor applications, and test reactor irradiation of some Mo-alloys has led to conclusions that irradiation embrittlement is potentially a limiting issue. That irradiation test program also indicates that high purity Mo may retain residual ductility, though small, and provides ideas for further improvements [5,6]. Adopting Mo-alloys for light water reactor applications faces many other challenges including thin-wall tube fabrication, corrosion, and oxidation resistance, as Mo has been known to be susceptible to corrosion and oxidation in oxidizing environments; Mo will form volatile MoO_3 with oxygen at temperatures > ~800°C.

An ATF cladding design developed with coated Mo-alloy cladding utilizes molybdenum's high strength at temperatures up to ~1,500°C to maintain fuel rod integrity and core coolability during a severe accident. The outer surface is coated with a thin, metallurgically bonded Zr-alloy or Al-containing stainless steel (FeCrAl) to provide corrosion resistance in LWR coolants during normal operation and oxidation resistance during severe accidents.

The fully metallic Mo–Zr and Mo–FeCrAl duplex claddings are anticipated to achieve accident tolerance by forming a

protective oxide during an accident. The thin Zr-alloy coating will be completely oxidized to ZrO_2 as the temperature reaches $1,000^\circ C$ or higher. With proper alloying, the ZrO_2 will maintain its integrity and stability and provide protection to the underlining Mo-alloy. A thin FeCrAl coating is highly corrosion resistant in LWR coolants due to formation of a chromium-rich protective oxide, mainly Cr_2O_3 . In high temperature steam, FeCrAl is highly corrosion resistant due to the formation of a thin aluminum rich oxide, Al_2O_3 . ZrO_2 and Al_2O_3 are stable in steam and steam enriched with hydrogen to temperatures $>1,500^\circ C$. However, the actual temperatures that the oxides will protect the Mo cladding will depend on factors, such as integrity of the ZrO_2 and interdiffusion between the metal coating and Mo. Triplex cladding with a liner of Zr- or Nb-alloy on the inner surface is an optional design, if additional resistance to attack by fission products or higher toughness is needed. A schematic of the duplex and triplex coated Mo-alloy cladding design is shown in Fig. 1.

In this ATF cladding design, the thickness of the Mo-alloy cladding will be limited to ~10 mils (0.25 mm) to reduce its impact on neutron absorption. The coating thickness of Zr-alloy and FeCrAl will be in the range of ~ 1–4 mL. Fuel rods with coated Mo-alloy cladding will be fabricated with conventional UO_2 fuel pellets used in current commercial designs. Our preliminary neutronic analysis indicates that fuel assemblies with desired reactivity for 18 month and 24 month cycle length can be achieved with 5% enriched fuel by adjusting the distribution of burnable poison rods, and slightly increasing the average enrichment [7].

2. Feasibility study of coated Mo-alloy cladding

2.1. Fabrication of thin wall Mo-alloy tubes and improvement of mechanical properties

Thin wall Mo alloy cladding suitable for LWR applications was not commercially available, and fabricators having experience in Mo-alloy have been very limited mainly due to the fact that mechanical formation of Mo and many other refractory metals need to be performed at certain elevated temperatures. For fabrication of Mo-alloy tubes, a minimum temperature of $300^\circ C$ is required. Under this ATF program, thin wall Mo-alloy tubes with an outer diameter of 9.4 mm or 10 mm (0.37 inches

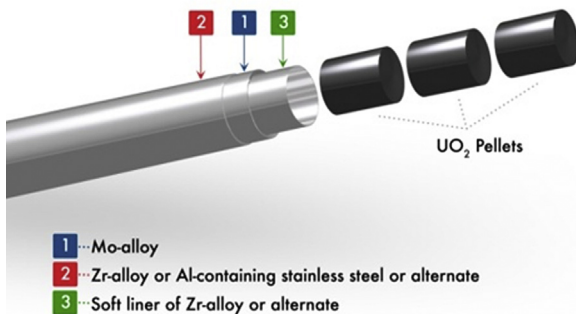


Fig. 1 – Schematic of coated Mo-alloy cladding.

Table 1 – Tensile properties of partially recrystallized Mo-alloy tubes with 0.2 mm wall thickness.

Tensile property (1.5" gauge length), room temperature			
Mo partial recrystallization			
	PM	LCAC	ML-DOS
0.2% yield, (ksi/Mpa)	73.5 (507)	82.4 (568)	90 (623)
UTS, (ksi/Mpa)	80.1 (552)	85.4 (589)	92.2 (636)
Uniform elongation, %	17	16	20
Total elongation, %	52	39	43
Tensile property (1.5" gauge length), 320°			
PM Mo partial recrystallization			
	1	2	3
0.2% yield, (ksi/Mpa)	44.5 (307)	50.6 (349)	53.7 (370)
UTS, (ksi/Mpa)	60.1 (415)	57.7 (398)	61 (421)
Uniform elongation, %	17	18	15
Total elongation, %	20	22	24

LCAC, low carbon arc cast; PM, power metallurgy.



Fig. 2 – A PM Mo tube sample tested at room temperature. PM, power metallurgy.

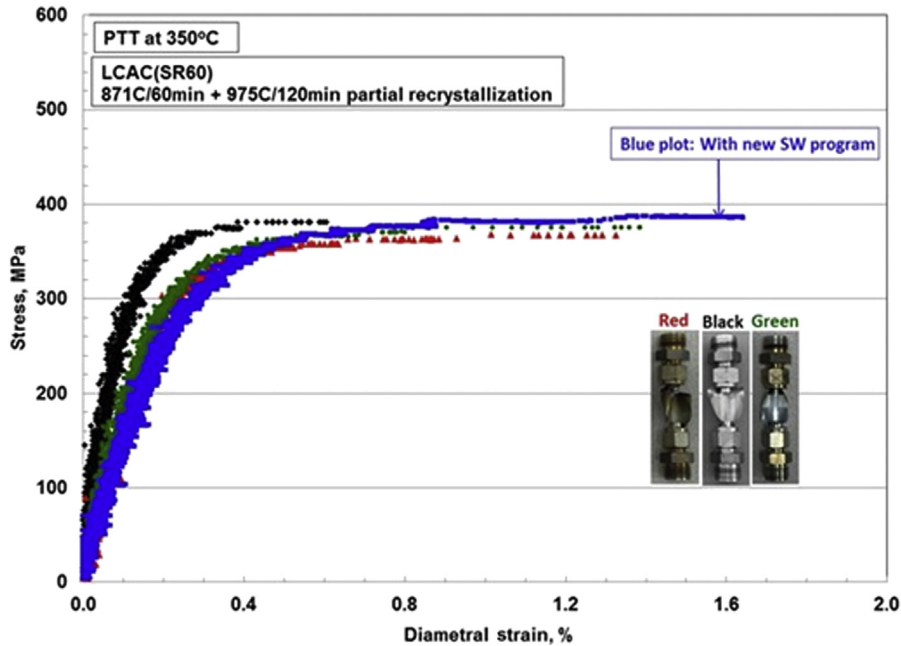


Fig. 3 – Failure strength as a function of diametral strain of partially recrystallized LCAC Mo tubes. LCAC, low carbon arc cast; PPT, Pressurized Tube Test.

or 0.40 inches) and wall thickness of 0.2–0.25 mm have been fabricated in lengths of 1.5 m (5 feet). Tubes have been made of pure Mo, including from low carbon arc cast (LCAC) and power metallurgy (PM) billets, as well as oxide dispersion strengthened, Mo-DOS, in which Mo is doped with dispersed La_2O_3 particles. Typical La_2O_3 concentration in weight is ~0.3%, but some tubes with 1% were fabricated. Excellent tube straightness and uniform wall thickness have been achieved.

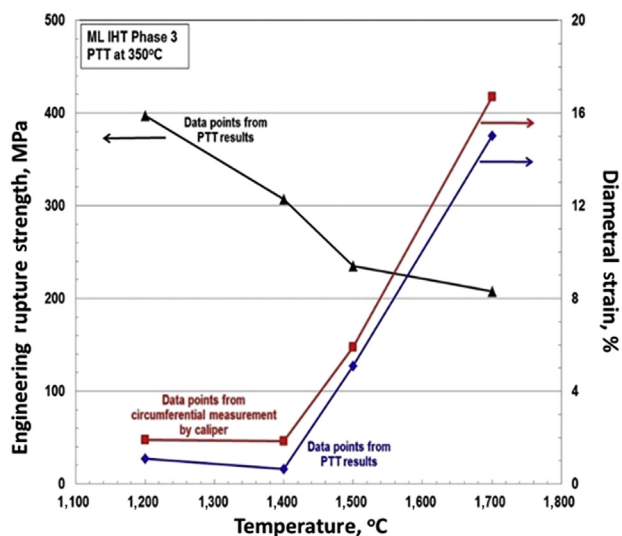


Fig. 4 – Failure strength and diametral ductility of Mo-DOS tubes after receiving an induction heat treatment with temperature shown in the X-axis. Mo-DOS, molybdenum oxide dispersion strengthened (ML: Mo-ODS, IHT: Induction Heat Treatment, PTT: Pressurized Tube Test).

The mechanical properties of the thin wall tubes are highly dependent on the final heat treatment condition. Most Mo alloy tubes have been used in stress relieved conditions with a final heat treatment at ~870°C. The stress relieved tubes can possess high strengths of >600 MPa, but the elongation or ductility in axial tensile test at 320°C test is generally low at < 10%. A series of tests were performed to determine the conditions for improved ductility. In partially recrystallized conditions, the yield and ultimate strength, and uniform and total elongation of tube samples with a gauge length of 3.8 cm (1.5 inch) are shown in Table 1. A typical tube sample tested at the room temperature is shown in Fig. 2. The ductility of partially recrystallized Mo-alloy tubes is comparable to that of Zr-alloy at the room temperature. At 320°C, the uniform elongation of Mo-alloy tubes is not changed, whereas the total elongation is somewhat reduced.

One common issue associated with high strength, thin wall tubes is their propensity to axially split. The tube diametral mechanical properties have been tested using a rig with the tube sample placed in a furnace for testing at temperatures up to 900°C. The test sample with a tube gauge length of 2.5 cm (1 inch) is pressurized with argon gas whereas the outer diameter is monitored continuously using a laser measurement system, which can record up to 100 data points per second. Fig. 3 shows preliminary results of the failure strength as a function of the diametral strain for samples from a tube made of LCAC. The tube samples were heat treated to a partially recrystallized condition. The diametral ductility at 350°C is low at ~1.5%. Recent tests on samples with modified heat treatment have now produced diametral strain of ~6% with strength of 350 MPa. Further refinement is in progress.

Optimizations of the mechanical properties of Mo-alloy cladding is an important effort of this initiative, because of

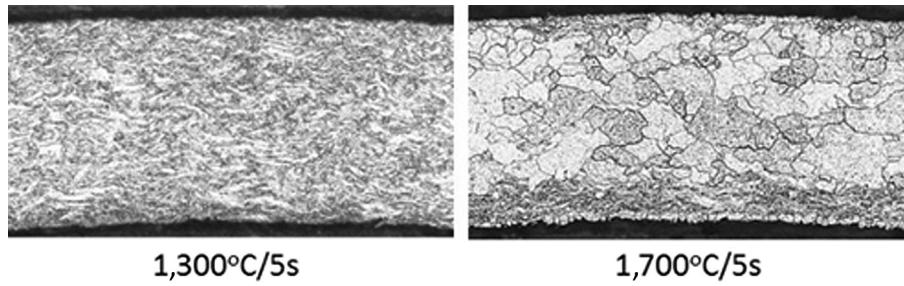


Fig. 5 – Grain microstructure of LCAC Mo tube samples after receiving an induction heat treatment at 1,300 and 1,700°C for 5 seconds. LCAC, low carbon arc cast.

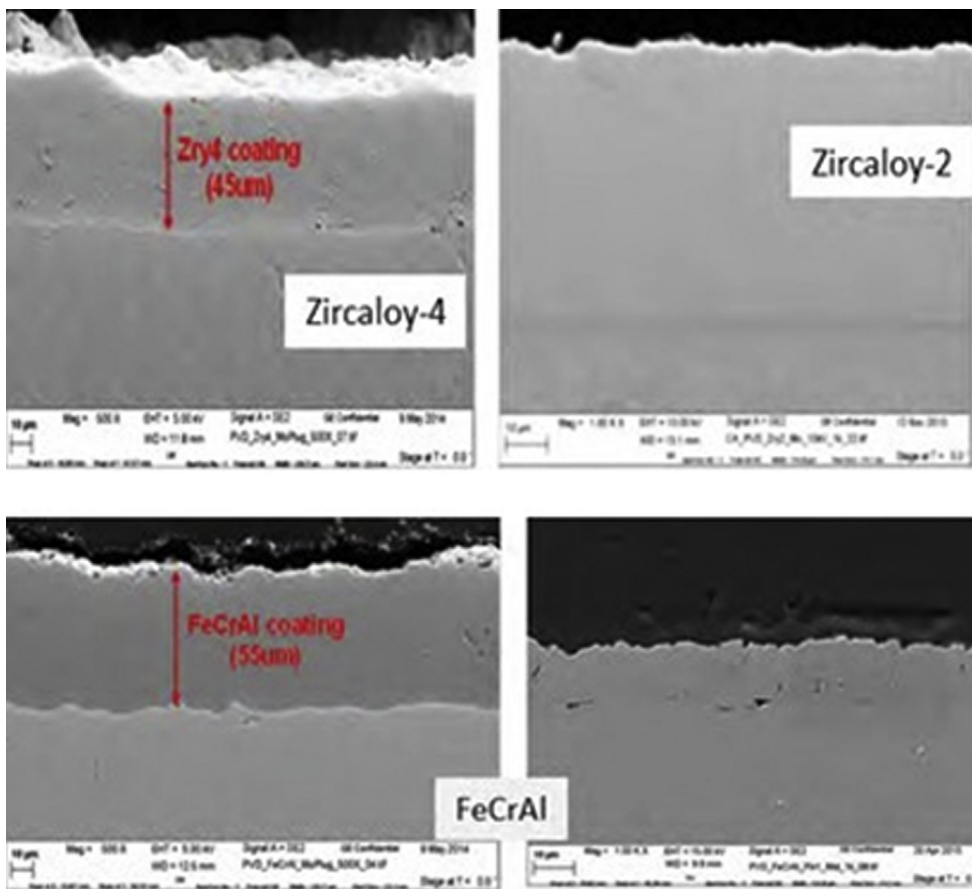


Fig. 6 – Examples of Zircaloy and FeCrAl coated on Mo-alloy tubes. FeCrAl, iron, chromium, and aluminum.

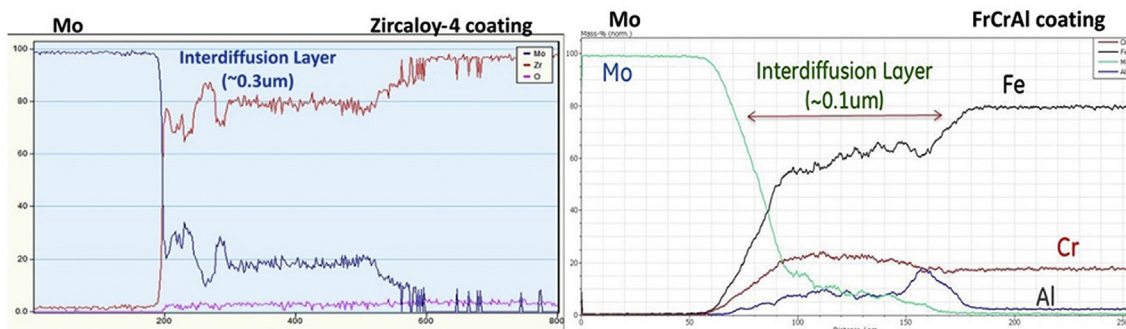


Fig. 7 – Elemental line scans of the interfaces between coating and Mo tube. FeCrAl, iron, chromium, and aluminum.

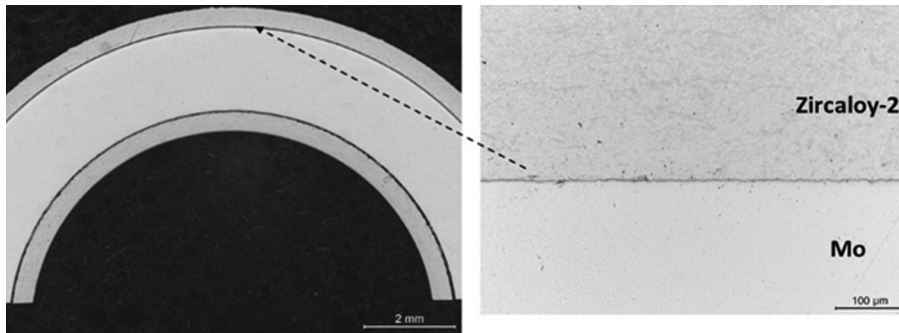


Fig. 8 – Zircaloy bonded to Mo tube outer and inner surfaces via hot hydrostatic pressing.

the concern regarding irradiation embrittlement. It has been reported that part of the embrittlement results from grain boundary weakness due to segregation of oxygen and possibly other species to grain boundaries. For reference, the specification for oxygen content in current Mo is typically 40 ppm, with LCAC Mo having lower oxygen than PM Mo. Two efforts have been undertaken: (1) controlling the microstructure of the finished tubes; and (2) addition of minor alloying elements which may strengthen the grain boundary [5]. For the second approach, new alloys containing Al, B, Zr, and Si are being fabricated. For microstructure control, an induction heat treatment facility has been established to heat treat tube samples to temperatures as high as 1,700°C within 1–2 seconds and hold the temperature constant for a short duration. The induction heat treatment is aimed at: (1) forming very fine, equi-axed grains; and (2) preventing grain boundary segregation of impurities. Small grain size has been reported to increase both the strength and ductility of molybdenum [8].

Fig. 4 shows the 350°C engineering rupture strength of Mo-DOS tubes (0.25 m wall thickness) and diametral strain as a function of the induction heat treatment temperature. Fig. 5 shows the microstructures. It can be seen that significant increase in the diametral ductility to 16% can be achieved with corresponding reduction in the failure strength to 200 MPa.

2.2. Surface coating for corrosion and oxidation protection

Coating on molybdenum is an optional means to protect molybdenum, due to the lack of existing technical basis for alloying Mo to improve its corrosion and oxidation resistance. A limited effort of evaluating corrosion resistant Mo alloys, such as Mo–Nb binary alloys, has been explored in parallel. Surface coating can be formed via deposition from vapors or powder or thermal-mechanical forming. An important requirement for surface coating is to form a metallurgical bonding between the coating and Mo to ensure durability of the coating under various operational conditions, including pellet-clad mechanical interaction (PCMI) and thermal cycling.

Coating of Zr-alloy and FeCrAl by deposition on Mo-alloy tubes was studied using various techniques including: cold spray, vacuum plasma spray (VPS), high velocity oxygen fuel (HVOF) spray, high velocity air fuel (HVOF) spray, and several

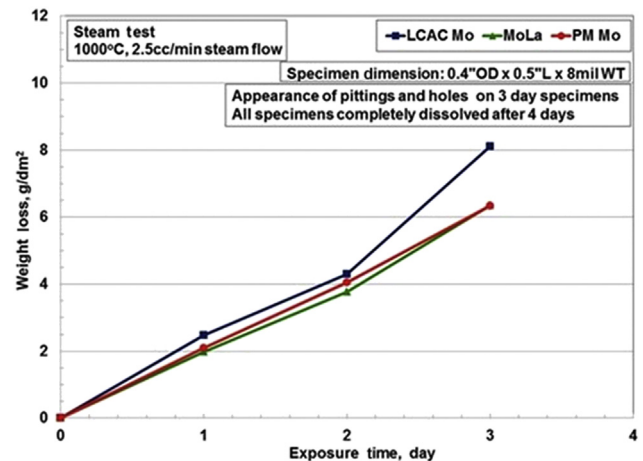


Fig. 9 – Weight loss of bare Mo tube as a function test time in 1,000°C flowing steam.

physical vapor deposition techniques (PVD). The spray coating techniques (VPS, HVOF, HVOF) use fine metal particles, which creates safety concerns particularly with Zr-alloy powders. PVD transports material from a solid target material onto the Mo tube surface in a high vacuum system. Three PVD techniques were evaluated, and cathode arc physical vapor deposition or CA-PVD has been found to achieve the deposited layer with: (1) good thickness uniformity; (2) excellent adhesion of the coating to the Mo tube; and (3) excellent metal density with no visible porosity of the coating. Tube samples, 8 cm or longer have been prepared with CA-PVD, and scaling up in length appears feasible, but the process is inherently expensive. Examples of coated Mo tubes are shown in Fig. 6.

The adhesion of FeCrAl or Zircaloy coating to the Mo tube is due to the formation of a sub-micrometer interdiffusion zone at the interface during the CA-PVD coating process, as shown in Fig. 7. The interdiffusion zones are in the range of 0.1–0.3 μm. To date, > 100 tube samples of each coating type have been fabricated and none has experienced coating delamination.

For commercial scale production, the feasibility of thermal-mechanical forming of coated tubes has been explored. There has not been prior arts in informing coating on Mo-alloy. Due to the high strength and high work hardening rate

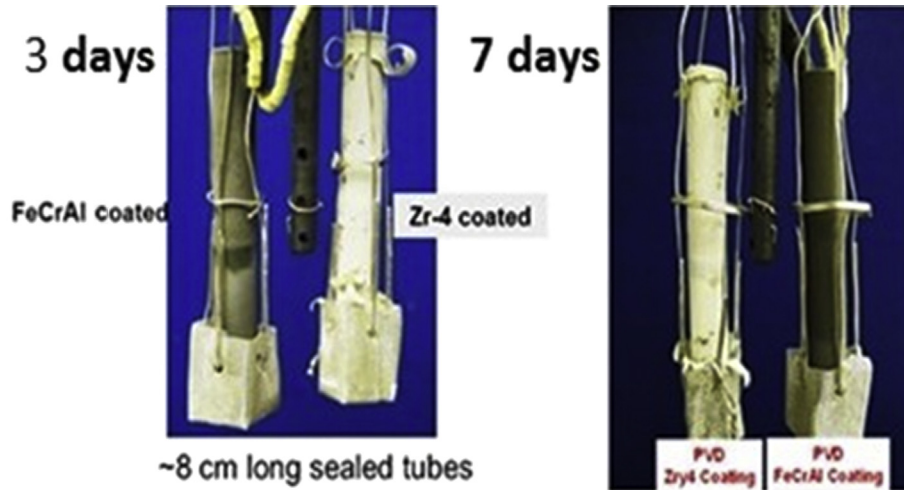


Fig. 10 – Coated Mo rodlets tested in 1,000°C for 3 days and 7 days. FeCrAl, iron, chromium, and aluminum.

of Mo-alloys, mechanical forming of coated Mo-alloy tube with metallurgical binding presents a highly challenging task. Two approaches have been initiated to demonstrate the feasibility of mechanical forming for coated Mo-alloy tubes: (1) hot coextrusion; and (2) hot isostatic pressing (HIPing or hip-ping). A series of hip-ping conditions has been planned. The first hip-ping performed at 1,000–1,100°C has produced encouraging results for forming a bonded Zircaloy-2 on both the outer and inner surface of an Mo-alloy tube, as shown in Fig. 8. Bonding of a three-layer configuration with Zircaloy on niobium and then on Mo-alloy was also achieved. However, bonding of FeCrAl on an Mo-alloy tube has yet been achieved, and additional hip-ping trials have been planned.

2.3. Corrosion and oxidation resistance of coated and uncoated Mo-alloy

The corrosion of bare Mo in simulated LWR water results in metal loss with time. The mechanism has not been evaluated, but is likely a result of forming a soluble molybdenum oxide. Therefore, coating with corrosion resistant material, such as Zr-alloy or stainless steel is needed. It has been found that

adding Nb in high concentrations to Mo can significantly reduce the corrosion rate in simulated LWR water [9] and some Mo–Nb alloy samples are being prepared for further testing.

The oxidation rate of bare Mo is highly sensitive to free oxygen in the test environment. In a loss of coolant accident, it is expected that the steam in the reactor core will be highly enriched by hydrogen due to oxidation of various components. Tests performed in pure steam are considered to be conservative for estimation of the behavior of ATF cladding. It is also recognized that pure steam will dissociate into hydrogen and oxygen, and based on thermal equilibrium calculations, ~1,400 wt. ppm and 174 wt. ppm of oxygen and hydrogen will be present in steam in equilibrium at 1,200°C. Fig. 9 shows the oxidation or weight loss rate of bare Mo tube samples tested in 1,000°C steam for 1 day, 2 days, and 3 days. The oxidation rate is ~20 μm per day, which is <1% of the oxidation rate of Zr-alloy. However, the oxidation rate is expected to increase significantly when the temperature increases as the oxygen content in the test steam increases.

Surface coating with FeCrAl or Zr-alloy is necessary to protect Mo from oxidation at elevated temperatures. Fig. 10

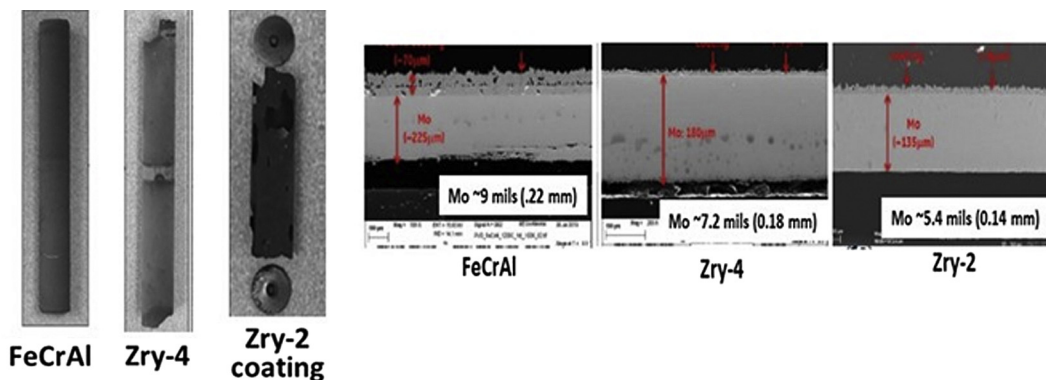


Fig. 11 – Coated Mo rodlets tested in 1,200°C for 24 hours. FeCrAl, iron, chromium, and aluminum.

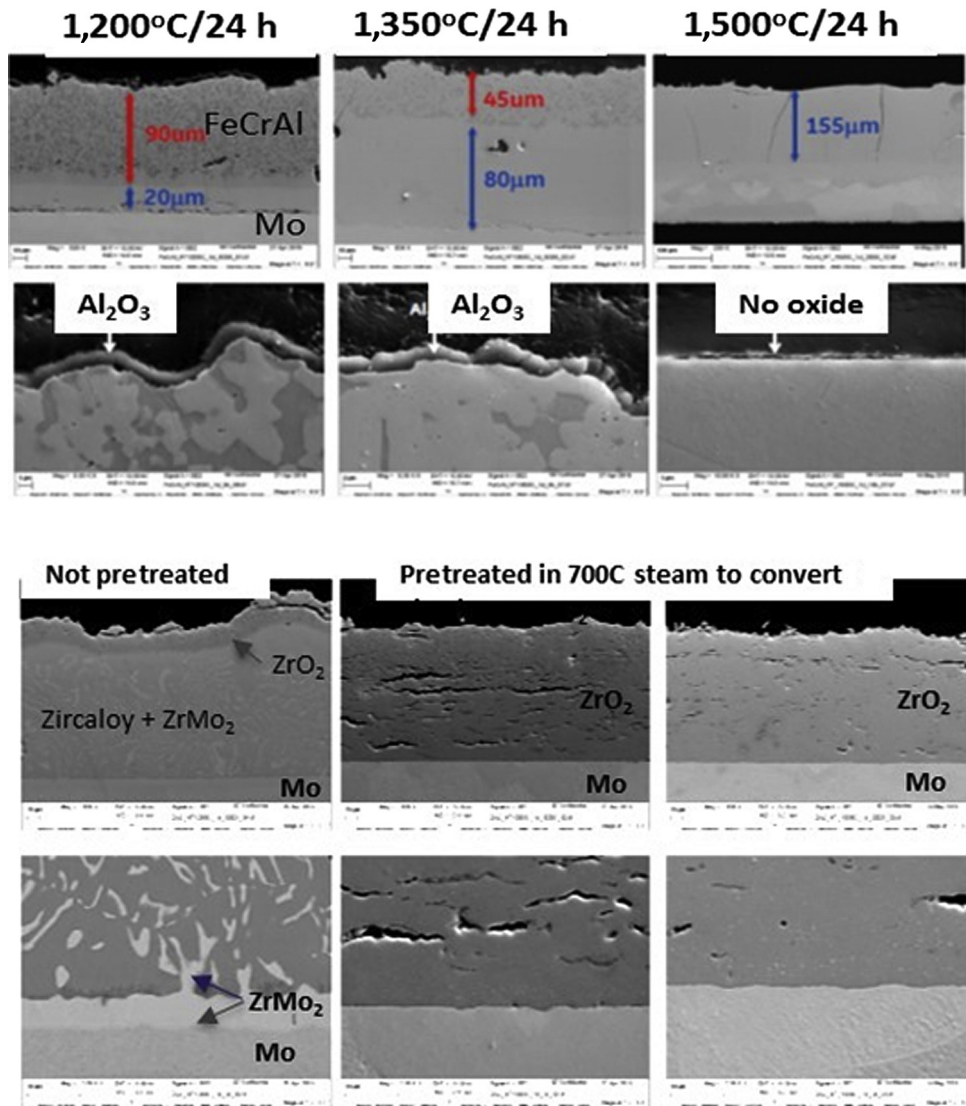


Fig. 12 – Coated Mo tube samples tested in a furnace with flowing argon gas; Zircaloy coated samples for 1,350 and 1,500°C test was preoxidized in 700°C steam for 24 hours. FeCrAl, iron, chromium, and aluminum.

shows coated Mo-alloy tubes after testing in 1,000°C steam for 3 days and 7 days. The tube samples are 10 cm (4 inch) long with both ends welded to Mo endcaps before being coated by CA-PVD. The FeCrAl coated Mo tubes survived for 7 days with no indication of any damage. The Zircaloy-2 coated tubes also survived tests to 7 days, but the ZrO_2 had extensive spallation.

Fig. 11 shows coated Mo tubes tested in 1,200°C steam for 24 hours. Again, the FeCrAl tube shows excellent oxidation resistance with no damage. The Zircaloy-2 and Zircaloy-4 coated tubes show extensive oxide spallation and breakage of the endcaps, but 60–90% of the Mo tube remain intact.

The spallation of ZrO_2 in the tests is worse than anticipated, as oxide formed on Zr-alloy cladding after standard LOCA tests normally would maintain some integrity. An analysis of the alloy chemistry of the Zr-alloy coatings found that more than half of the very low alloying elements Cr, Fe, Ni, and Sn added to improve the corrosion resistance of

Zircaloy actually were lost in the CA-PVD process. The Al content in the FeCrAl coating was found to be only approximately half of that in the original FeCrAl target material of 6%. The low concentration of alloying elements in the Zircaloy coatings is believed to have reduced the corrosion resistance and increased susceptibility to oxide spallation. Additional coated Mo tube samples are under fabrication for testing. Current commercial Zr-alloys as well as advanced Zr alloys will be used for future tests.

The thermal stability of the coatings or interdiffusion of Mo and the coating materials, i.e., Zr, or Fe, Cr, and Al, is a subject of interest, as interdiffusion has the potential of degrading the protectiveness of the coatings. The interdiffusion study was carried out in a furnace flooded with flowing argon gas to avoid excessive oxidation of open-ended Mo tube inner surface or the coating.

Zircaloy-2 and FeCrAl coated samples were tested at 1,200°C for 24 hours. For higher temperatures, Zircaloy-2

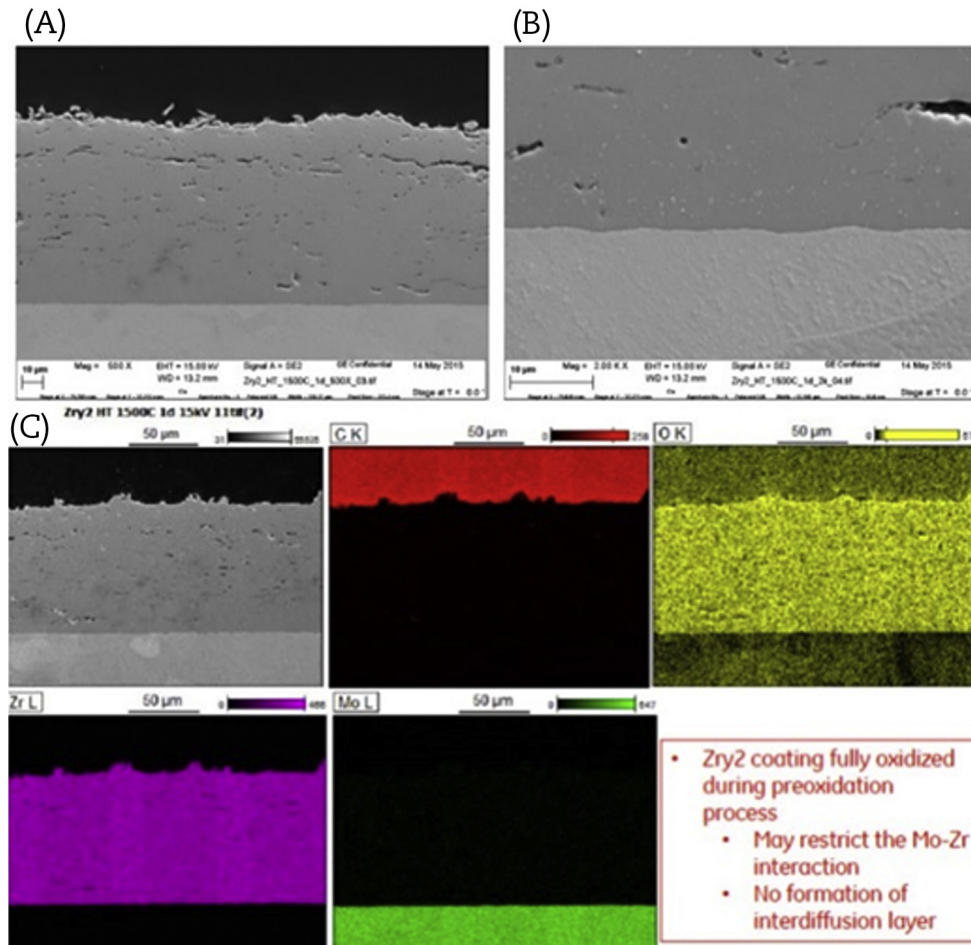


Fig. 13 – Cross-section view and elemental mapping of Mo tube sample with preoxidized Zircaloy coating tested at 1,500°C for 24 hours.

coated tube samples were first preoxidized in 700°C steam for 1 day to convert the Zircaloy-2 coating into ZrO_2 . The preoxidized Zircaloy-2 and FeCrAl coated samples were placed in the furnace at 1,350 and 1,500°C for 24 hours.

Fig. 12 shows the formation of a thin protective Al_2O_3 of ~3 μm at 1,200 and 1,350°C on the outer surface even in a flowing argon environment, which normally would contain low oxygen contamination. However, no protective Al_2O_3 was found at 1,500°C. Another observation is the diffusion of Mo into the FeCrAl coating forming complex Mo-enriched phases. Thus, it is evident that the capability of the FeCrAl is limited to ~1,350°C. But, that may be achieved only if diffusion of Mo will not impact the stability of the protective Al_2O_3 film in steam environments. As shown above, steam testing thus far confirms that FeCrAl coating is capable of protecting Mo cladding in 1,200°C for 24 hours.

The Zircaloy-2 coated sample also shows significant diffusion of Mo into the Zircaloy coating to form $ZrMo_2$ at 1,200°C in 24 hours, and a thin ZrO_2 forms on the coating outer surface. Once the Zr-alloy coating is converted to ZrO_2 , the oxide stays quite stable on the Mo-alloy cladding surface for 24 hours at 1,350°C and 1,500°C, as shown in Figs. 12 and 13. The lack of interaction between Mo metal and ZrO_2 is anticipated and is the basis of the current design concept, as ZrO_2 is

highly stable and hence transfer of oxygen to Mo should not occur because Mo has low oxygen affinity and solubility. The results indicate that Zr-alloy coated Mo tubes may achieve oxidation protection to higher temperatures if: (1) the Zr-alloy coating is completely converted to ZrO_2 at temperatures < ~1,000°C; and (2) the integrity of ZrO_2 is maintained. Both need to be fully demonstrated.

2.4. Irradiation properties

A potentially limiting property of Mo-alloy is irradiation-induced embrittlement. It has been identified from earlier tests in a fast reactor that irradiation may cause grain boundary weakness and significantly reduce the ductility of Mo-alloys [6]. Irradiation data from tests in light water reactors do not exist. However, irradiated Mo cladding rings and thin disks achieving a burnup of 112 GWd/MTU at the Halden Reactor have recently been made available to our project for postirradiation examination (PIE).

The Halden test was aimed at evaluating the thermal conductivity of UO_2 and $(Pu,U)O_2$ thin wafer. The test used pure Mo cladding rings, made of PM Mo, of 0.9 mm high and 0.5 mm thick to contain fuel wafer having 20% enrichment, and Mo disks of 3.2 mm thick to separate fuel pellets. A total of

300 Mo–UO₂ sets were irradiated to 112 GWd/MTU under heat fluxes of 2–4 times that of the current LWR fuel rods. While PIE is still underway, initial data indicate some useful information, such as: (1) the Mo cladding ring was strong enough to contain 7% fuel volume swelling forcing the fuel pellet to expand vertically; and (2) the irradiated Mo was resistant to chemical attack by fission products. However, brittle fracture of the Mo ring was observed under a strong impact force during defueling. The PIE data will be reported when examination is completed.

Future irradiation tests will be needed to evaluate the validity of the countermeasures for irradiation embrittlement, which include: (1) improvements in the diametral ductility of Mo-alloy cladding through heat treatment and microstructural control; and (2) minor addition of alloying elements for grain boundary strengthening.

Fabrication has been in progress to provide rodlets with coated Mo cladding for irradiation at the Advanced Test Reactor (ATR) and the Halden Reactor over the 2015–2017 time frame. Welding of Mo cladding to endcaps have been successfully developed using electron beam (EB) welding and several other techniques [7]. Development of solid state joining using resistant projection welding or equivalent to avoid large grain growth at the welded zone has also been underway.

3. Summary

The goal of this initiative is to demonstrate the feasibility of developing coated Mo-alloy cladding for LWR fuel cladding to enhance the accident tolerance of fuel rods in several loss of coolant accidents. The target is to demonstrate that coated Mo-alloy cladding can meet: (1) performance and reliability requirements for normal operation; (2) licensing safety requirements during power transients; and (3) significantly enhanced tolerance to severe accidents. A measurable goal is to demonstrate that the coated Mo-alloy cladding can survive in a steam environment at 1,200–1,500°C for at least 24 hours.

Many first of its kind technical approaches have been undertaken, including fabrication of very thin walled Mo-alloy tubes of 0.20–0.25 mm thickness and induction heat treatment of the thin wall tubes to define the optimum heat treatment conditions for improving the diametral ductility, which is ultimately important for nuclear fuel cladding.

Surface coating using CA-PVD has been demonstrated to form metallurgical bonding between the Zr-alloy or FeCrAl deposits and the Mo-alloy tube. The metallurgical bonding will ensure integrity of the coating under severe service conditions. For commercial scale production of coated tubes, mechanical forming by hiping has shown the feasibility of forming good bonding between Mo–Zr and Mo–Nb–Zr interfaces, and fabrication of test tubes using hiping are under development. Further studies to produce coated Mo-alloy tubes with hiping, coextrusion, pilgering, drawing, and their combinations are underway. The target is to produce coated Mo-alloy tubes with a diametral ductility of ~10% before irradiation.

Coated Mo-alloy cladding with FeCrAl and Zr-alloy has been demonstrated to be capable of completely or partially surviving in 1,200°C for 24 hours. Additional tests are underway at

temperatures >1,200°C to establish the maximum protection limits. Corrosion resistance of coated Mo-alloy tubes in simulated light water reactor coolants will need further tests to confirm that the cladding will meet the stringent requirements for normal operation. As a further enhancement in corrosion performance, evaluation of the characteristics and fabricability of Mo–Nb alloys has been initiated.

Irradiation tests of coated Mo-alloy cladding have been under preparation to begin at ATR and Halden Reactor in 2016–17. Irradiation tests of Mo-alloys designed for grain boundary strengthening as well as Mo-alloy samples receiving induction heat treated to possibly minimize grain boundary segregation will be performed to evaluate the availability of sufficient margins to meet the mechanical property requirements.

Conflicts of interest

All authors have no conflicts of interest to declare.

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REFERENCES

- [1] B. Cheng, Fuel behavior in severe accidents and Mo-alloy based cladding to improve accident tolerance, Paper #A0034, TopFuel, Birmingham, UK, 2012.
- [2] S. Bragg Sitten, Application of MELCOR to ATF Concepts for Severe Accident Analysis, Presented at EPRI/INL/DOE Workshop on Accident Tolerant Fuel, San Antonio, February 27, 2014.
- [3] B. Cheng, P. Chou, Y. J. Kim, Feasibility evaluations of Mo-alloy cladding to enhance accident tolerance, Paper #0204, TopFuel, Zurich (Switzerland), September 14, 2015.
- [4] IAEA Symposium on Accident Tolerant Fuel Concepts for Light Water Reactors, Oak Ridge National Laboratory, Tennessee, USA, Oct. 13–16, 2014 (Proceedings to be published by IAEA).
- [5] B.V. Cockeram, R.W. Smith, K.J. Leonard, T.S. Byun, L.L. Snead, Irradiation hardening in unalloyed and ODS molybdenum during low dose neutron irradiation at 300° C and 600° C, *J. Nucl. Mater.* 382 (2008) 1–23.
- [6] T.S. Byun, M. Li, B.V. Cockeram, L. Snead, Deformation and fracture properties in neutron irradiated pure Mo and Mo alloys, *J. Nucl. Mater.* 376 (2008) 240–246.
- [7] B. Cheng, P. Chou, Y.-J. Kim, Characterization of Coated Molybdenum-alloy Cladding for Accident-tolerant Fuel, Progress Report, EPRI, Palo Alto (CA), 2015, p. 3002005557.
- [8] G. Liu, G.J. Zhang, F. Jiang, X.J. Sun, J. Sun, Nanostructured high-strength molybdenum alloys with unprecedented tensile ductility, *Nat. Mater.* 12 (2013) 344–350.
- [9] Y.-J. Kim, B. Cheng, P. Chou, Steam oxidation behavior of protective coatings on LWR molybdenum cladding for enhancing accident tolerance at high temperatures, Paper #A0172, TopFuel, Zurich (Switzerland), September, 2015.