REGULAR ARTICLE

Evaluations of Mo-alloy for light water reactor fuel cladding to enhance accident tolerance

Bo Cheng[1*], Peter Chou[1], and Young-Jin Kim[2]

[1] Electric Power Research Institute (EPRI), Palo Alto, CA 94304, USA
[2] GE Global Research Center, Schenectady, NY 12309, USA

Abstract. Molybdenum based alloy is selected as a candidate to enhance tolerance of fuel to severe loss of coolant accidents due to its high melting temperature of ∼2600 °C and ability to maintain sufficient mechanical strength at temperatures exceeding 1200 °C. An outer layer of either a Zr-alloy or Al-containing stainless steel is designed to provide corrosion resistance under normal operation and oxidation resistance in steam exceeding 1000 °C for 24 hours under severe loss of coolant accidents. Due to its higher neutron absorption cross-sections, the Mo-alloy cladding is designed to be less than half the thickness of the current Zr-alloy cladding. A feasibility study has been undertaken to demonstrate (1) fabricability of long, thin wall Mo-alloy tubes, (2) formability of a protective outer coating, (3) weldability of Mo tube to endcaps, (4) corrosion resistance in autoclaves with simulated LWR coolant, (5) oxidation resistance to steam at 1000–1500 °C, and (6) sufficient axial and diametral strength and ductility. High purity Mo as well as Mo + La_2O_3 ODS alloy have been successfully fabricated into ∼2-meter long tubes for the feasibility study. Preliminary results are encouraging, and hence rodlets with Mo-alloy cladding containing fuel pellets have been under preparation for irradiation at the Advanced Test Reactor (ATR) in Idaho National Laboratory. Additional efforts are underway to enhance the Mo cladding mechanical properties via process optimization. Oxidation tests to temperatures up to 1500 °C, and burst and creep tests up to 1000 °C are also underway. In addition, some Mo disks in close contact with UO_2 from a previous irradiation program (to >100 GWd/MTU) at the Halden Reactor have been subjected to post-irradiation examination to evaluate the chemical compatibility of Mo with irradiated UO_2 and fission products. This paper will provide an update on results from the feasibility study and discuss the attributes of the coated Mo cladding design to meet the challenging requirements for improving fuel tolerance to severe loss of coolant accidents.

1 Introduction

Zr-based alloys have served as the fuel cladding for light water reactors due to unique combination of low neutron cross-section, adequate corrosion resistance and mechanical properties. The reliability of Zr-alloy cladding has been steadily improved over the last five decades and has reached an excellent status in recent years. The Fukushima Daiichi accident triggered by the tsunami following an earthquake has illustrated the vulnerability of Zr-alloys to rapid steam oxidation during a severe accident when the flow of coolant into the reactor core is interrupted. Without availability of coolant flow to remove the nuclear decay heat, the fuel cladding temperature will rise rapidly. At temperatures exceeding 700–1000 °C, depending on the steam pressure, exothermic reaction of Zr with steam will release hydrogen and enthalpy or heat when ZrO_2 is formed. Due to the high

packing density of fuel rods in reactor cores, where a typical size core may have ∼50,000 fuel rods, the total heat from zirconium oxidation may exceed that of the nuclear decay heat, if oxidation heat is all released within a short duration of an hour or so. The excessive oxidation heat may contribute to earlier melting of some reactor core components and subsequently the fuel pellets. The amount of hydrogen generated by zirconium oxidation can be in the order of exceeding 1,000 kg, and, hence, can complicate efforts by plant operators to recover the cooling system to stabilize the plant [1].

For current LWRs, it is most essential to maintain availability of coolant flow into the core under any accident conditions, and the FLEX program initiated by the US NRC is targeted to achieving that objective. Another potential defense is to replace the zirconium alloy fuel cladding with another material having substantially higher resistance to steam oxidation and capability of maintaining fuel rod integrity at elevated temperatures, which may provide meaningful coping time for plant operators to
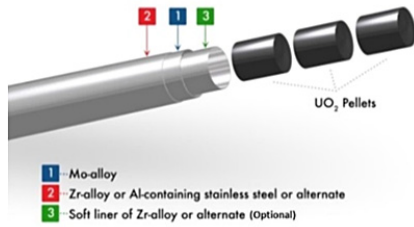
* e-mail: bcheng@epri.com

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

restore the core cooling systems [2,3]. The US Department of Energy (DOE) launched a multi-year 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 last 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 conceptual designs of coated molybdenum alloy cladding by utilizing the high temperature strength (1500 °C and beyond) of molybdenum to maintain core geometry for coolability during a design based and beyond the design based loss of coolant accidents, as illustrated in Figure 1 [1,3]. Metallurgically bonded surface coating with Al-containing stainless steel or Zr-alloy is to provide corrosion resistance during normal operation and steam oxidation resistance during loss of coolant accident with a target of surviving in steam at 1200–1500 °C for at least 24 hours. The inner surface may have a soft liner layer as an option, but its need will be determined following completion of the feasibility study.

This paper outlines the scope of the feasibility study for coated Mo-alloy cladding and shares the results obtained to date, as well as discusses the challenges ahead for completion of the feasibility study.

2 Scope of feasibility study and results

The feasibility study focuses on the following topics:

– fabricate Mo-alloy tubes with 0.2–0.25 mm wall thickness and characterize mechanical properties;
– form metallurgically bonded coating with Al-containing stainless steel or Zr-alloy of ~0.05 mm;
– weld Mo-alloy tube to endcaps;
– characterize corrosion resistance of coated and uncoated Mo-alloy tubes in autoclaves with simulated LWR coolants;
– characterize steam oxidation of coated and uncoated Mo-alloy tubes in steam at 1000–1500 °C.

Rodlets with coated Mo-alloy cladding containing enriched fuel pellets are also being fabricated for irradiation at the ATR reactor under funding by the US DOE and the Halden Reactor under its base program funding. Post-irradiation characterization of high purity Mo disks and cladding rings which were previously irradiated to high burnup at the Halden Reactor is also included in this feasibility study.

The effects of higher neutronic absorption cross-sections of Mo on fuel economics and fuel cycle designs were assessed and reported previously [1].

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

Mo-based alloys have been used in reducing environments as containers or thermocouples at elevated high temperatures as high as ~2000 °C. An extensive test program was undertaken by Bettis and Oak Ridge National Laboratories to evaluate the irradiation properties of various Mo-alloys in coupon forms for potential space reactor fuel material applications [5,6]. Thin wall Mo-alloy cladding suitable for LWR applications was not previously available. Under this ATF program, thin wall Mo-alloy tubes with the outer diameter of 9.4 or 10 mm (0.37 or 0.40 inches) and wall thickness of 0.2–0.25 mm have been fabricated in length of 1.5 meters (5 ft). Tubes have been made of pure Mo, including from low carbon arc cast (LCAC) and powder metallurgy (PM) billets, as well as oxide dispersion strengthened Mo-alloy (Mo-DOS) in which Mo is doped with dispersed La$_2$O$_3$. Typical La$_2$O$_3$ concentration in weight is ~0.3%, but some tubes with 1% were fabricated. Both LCAC Mo and Mo-ODS were found to retain small residual ductility following irradiation performed by the Bettis/Oak Ridge Program. Excellent tube straightness and uniform wall thickness have been achieved (Fig. 2).

Because of its high melting temperature and single phase structure (i.e., absence of phase transition) until melting at ~2600 °C, the mechanical strength will be maintained to much higher temperatures than that of common structural alloys including Zr, Fe and Ni based alloys. Pure Mo can maintain tensile strength of ~69 MPa (~10 ksi) at 1500 °C, while most other alloys would have lost their strength below 1000 °C.

The thin wall Mo and Mo-ODS tubes can achieve a tensile strength of 500–600 MPa in partially recrystallized form with good axial fracture elongation of 20–25% when measured with 3.8 cm (1.5") gauge length tube at room temperature as shown in Table 1. The strength can be controlled at 250–500 MPa depending on the final annealing condition.

One common issue associated with high strength, thin wall tubes is their propensity to axial split. A test rig with internally pressurized argon gas has been developed to test the diametral properties, including the diametral failure strength and diametral strain and creep rate at temperatures
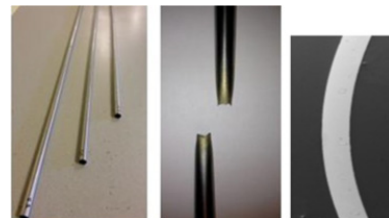

Fig. 2. Mo-alloy tubes with wall thickness of 0.2 mm and OD of 1.0 cm.

Table 1. Mechanical properties of partially recrystallized Mo-alloy tubes tested at room temperature.

Tensile property (1.5" gauge length), 320 °C		
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

up to 900 °C. Figure 3 illustrates the internally pressurized test results of samples of a partially recrystallized LCAC Mo tube. The measured diametral failure strength at 350 °C is ~380 MPa (55 ksi) and the diametral strain was measured as 1.4–16%.

Optimizations of the mechanical properties, particularly the diametral properties, are in progress via two approaches: firstly, modification of the tube thermo-mechanical reduction process and, secondly, controlling the microstructure of the finished tubes. For microstructure control, an induction heat treatment chamber has been set up to heat treat tube samples to various temperatures in the 1000–1700 °C range for 5–30 seconds, in order to determine the optimum heat treatment temperature for achieving the desired diametral and axial mechanical properties. Preliminary data show that diametral strain of 6–18% can be achieved at lower diametral strength.

Attempts have also been made to control the microstructure with very fine grain size, which has been reported to increase both the strength and ductility of molybdenum [7]. Data to date has indicated that rapid heat treatment and cooling via induction heat treatment cannot accomplish grain size control for high purity Mo or Mo-ODS. Further evaluation with alloying of the Mo matrix has been planned.

2.2 Formation of surface protective coating and interface stability

Molybdenum is susceptible to accelerated corrosion and oxidation in oxidizing environments at >~300 °C forming soluble and volatile MoO_3. Due to the lack of technical basis for alloying Mo to improve its corrosion and oxidation resistance at present, surface protection via a corrosion resistant outer layer, as depicted in Figure 1, has been pursued for this ATF design. A limited effort of evaluating corrosion resistant Mo-alloys, such as Mo-Nb binary alloys, has been explored in parallel.

FeCrAl alloys with ~20%Cr and ~6%Al has been known to possess excellent corrosion resistance in simulated LWR coolants relying on the formation of a protective Cr_2O_3, as well as excellent oxidation resistance in steam to ~1450 °C owing to the formation of a thin Al_2O_3 protective oxide. Zr-alloys can be optimized to possess excellent corrosion resistance in LWRs, and will convert to ZrO_2 rapidly at >1000 °C, which is expected to be stable in steam to protect the underlying Mo cladding.

This ATF project was designed to first prepare Mo-alloy tube samples with an outer protective layer utilizing suitable surface deposition techniques for various testing to
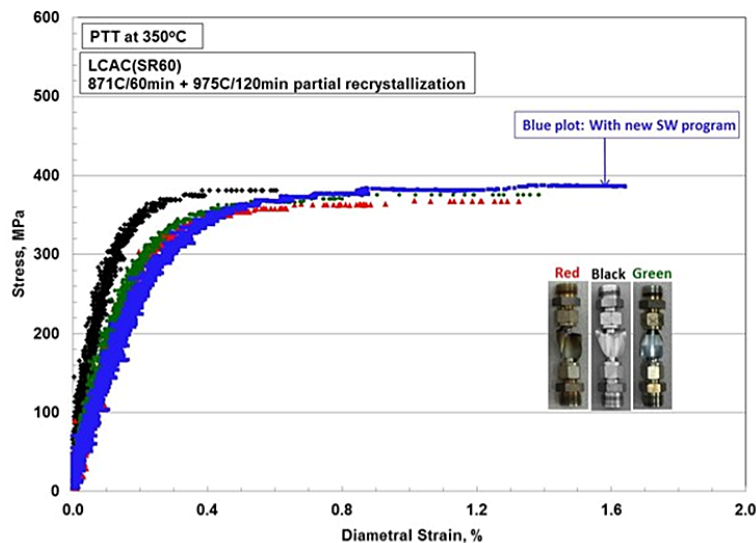
Fig. 3. Internally pressurized test of samples from a partially recrystallized LCAC Mo tube at 350 °C.
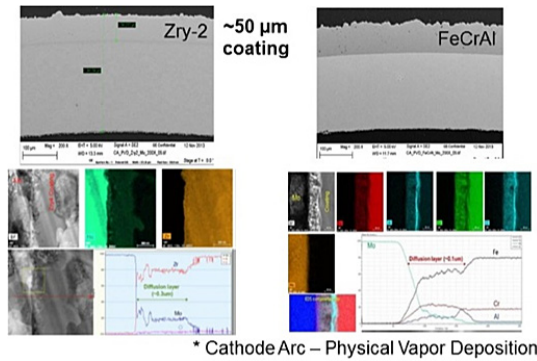
Fig. 4. Cross-section views of Mo tube with 0.2 mm wall thickness coated with a Zircaloy-2 or FeCrAl layer of ∼0.05 mm. The pictures at the bottom show the presence of an inter-diffusion layer of 0.3 and 0.1 μm at the interface of the Zircaloy-2 and FeCrAl coating, respectively [10].

demonstrate feasibility of the ATF design. Tasks have been implemented to evaluate the feasibility of mechanical co-reduction. The outer coating is required to form a metallurgical bonding with the Mo cladding in order to achieve integrity in all conditions.

Formation of a corrosion and oxidation resistant outer layer of Al-containing stainless steel or Zr-alloy have been successfully developed using various deposition techniques. Cathode Arc Physical Vapor Deposition, or CA-PVD, has been found to achieve the deposited layer with (1) excellent thickness uniformity, (2) excellent adhesion of the coating to the Mo tube, (3) excellent metal density with no visible porosity of the coating. Examples of CA-PVD coated Mo tubes are illustrated in Figure 4. It can be seen an inter-diffusion layer of 0.3 and 0.1 μm forms at the interface of the Zircaloy-2 and FeCrAl coating, respectively. The inter-diffusion layer provides excellent metallurgical bonding of the coated layer to the Mo tube. Figure 5 shows a uniform coating of FeCrAl formed on a welded Mo tube.

2.3 Tube to endcap welding

Mo tube to endcap welding has been successfully demonstrated via plasma and tungsten inert gas welding as well as electron beam (EB) welding. EB welding has been found to produce smaller weld and heat affected zones, as illustrated in Figure 6a, and has been used to fabricate rodlets for irradiation at the Advanced Test Reactor (ATR) in Idaho National Laboratory (INL).

Resistance projection welding has been demonstrated to fuse Mo tube to endcap at the interface without forming a
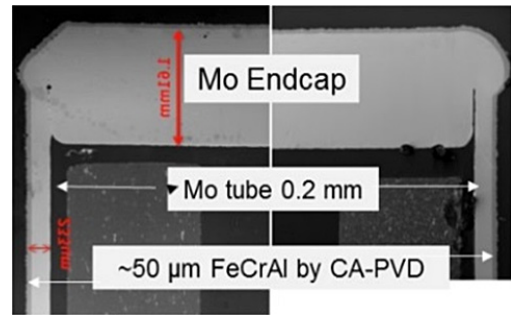
Fig. 5. Uniform FeCrAl coating thickness of 50 μm on a welded Mo tube (similar results for Zircaloy coating).
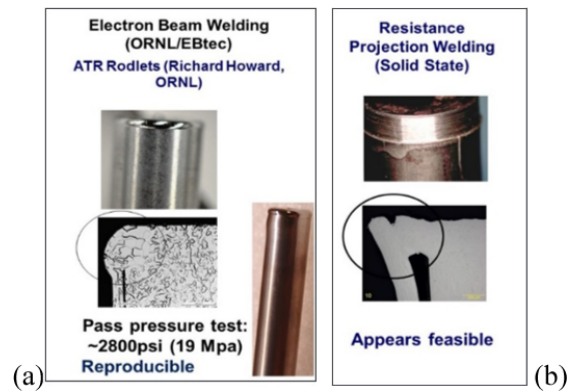
Fig. 6. Welded samples fabricated by (a) electron beam welding and (b) resistance projection welding.

fusion zone, as shown in Figure 6b. This technique is preferred for commercial deployment and will require further development.

2.4 Corrosion resistance in simulated LWR coolants

The corrosion resistance of pure Mo and Mo-ODS has been characterized in simulated BWR and PWR coolants at 288 and 330 °C, respectively, in long-term autoclave tests [8,9]. Table 2 summarizes the corrosion data in LWR coolants. It is noted that the corrosion resistance of bare Mo-alloys in simulated BWR and PWR environments is excessively high and hence will require protection with a coating of Zr-alloy or (Cr, Al)-containing stainless steel.

Preliminary results on Mo-alloys containing Nb have been found to significantly reduce the corrosion rate, as shown in Figure 7. Mo-alloy C containing 10% Nb has an

Table 2. Summary of the corrosion rate (in μm per month) of bare and coated Mo-alloy tubes in simulated LWR coolants.

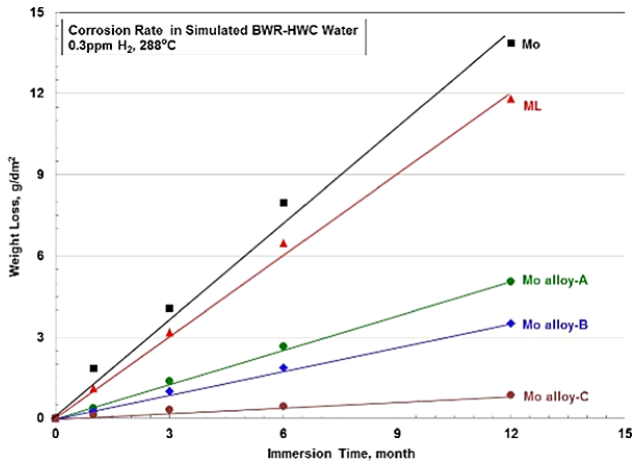| Test condition	Mo/ML	Zr-coated	FeCrAl-coated
PWR – 330 °C, 3.6 ppm H_2	∼5	Very low	Very low
BWR-HWC – 288 °C, 0.3 ppm H_2	∼9	Very low	Very low
BWR-HWC – 288 °C, 1 ppm O_2	∼40	Very low	Very low

Fig. 7. Corrosion resistance of pure and ODS Mo and Nb-containing Mo samples in simulated a BWR-HWC coolant.

order of magnitude lower corrosion rate ($\sim 0.5\,\mu m/mo$) than that of the bare, pure Mo tube in a simulated BWR water containing 0.3 ppm dissolved hydrogen.

2.5 Oxidation resistance in 1000–1500 °C steam

The oxidation resistance of uncoated Mo in oxidizing steam, i.e. steam containing free oxygen, has been known to be poor due to the formation of volatile MoO_3 at temperature $> \sim 600$ °C. In a severe loss of coolant accident, it is anticipated that the reactor core will have excess hydrogen due to corrosion and oxidation of various metallic components in the core. The Zr-alloy and FeCrAl coatings are to provide protection from steam oxidation at elevated temperatures.

In pure steam and steam plus 10% hydrogen at 1000 °C, uncoated Mo-alloy cladding has been found to have reasonable oxidation rate with a thicken loss of ~ 20–$25\,\mu m$ per day, which is two order of magnitude lower than that of Zr-alloys [9,10].

Coated Mo tubes with both-end welded received full protection from FeCrAl in 1000 °C for 7 days, shown in Figure 8. The Zircaloy-4 coated Mo tube showed delamination of the ZrO_2 and suffered some loss in the Mo wall thickness, but the Mo tube remains intact after 7 days.

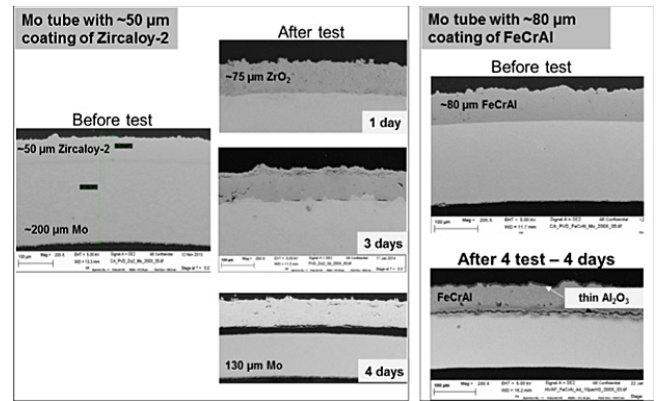Fig. 8. Mo tubes with both-ends welded to endcaps and coated with either FeCrAl or Zircaloy-4 after testing in 1000 °C steam for 7 days.

Fig. 9. Open-ended Mo-alloy tube samples with coating after oxidation test in 1000 °C for up to 4 days.

Figure 8 shows cross-sections of open-ended Mo tube samples coated with either Zircaloy-2 or FeCrAl after being tested in 1000 °C steam for up to 4 days. The Zircaloy-2 coated Mo tube shows the conversion of Zircaloy-2 to a dense ZrO_2 which protects the Mo tube from steam oxidation for up to 4 days. The good integrity of the oxide formed from Zircaloy-2 differs from the flaky oxide formed from Zircaloy-4 as shown in Figure 9.

Investigation of the integrity of the ZrO_2 oxide formed from the Zircaloy-4 coating in Figure 8 and Zircaloy-2 coating in Figure 9 has found that slightly over half of the alloying elements, Fe, Cr, Sn and Ni (Zircaloy-2 only), added to zirconium for corrosion and oxidation resistance were substantially lost during the CA-PVD coating process. This likely explains the flaky oxide observed in Figure 8. New target materials with substantially higher alloying concentrations have been obtained to improve the alloy chemistry of the coating. For the longer term, mechanical co-reduction should avoid the difficulty of controlling the alloy chemistry.

An interesting observation of the 1000 °C steam tested samples is the formation of an inter-diffusion zone in the FeCrAl-coated samples. The thickness was measured to be 2, 4, and 5 μm after 1, 3, and 7 days, respectively. Clearly, the inter-diffusion was not significant enough to impact the cladding integrity at 1000 °C for 7 days or much longer.

Tests in steam at 1200–1500 °C has been in process.

2.6 Irradiation properties

Previous irradiation tests have shown Mo and its alloys, like other metals and alloys, will suffer from irradiation embrittlement and the mechanism has been attributed to grain boundary weakness. It is anticipated that improving the diametral mechanical properties through process and microstructure optimization, as discussed above, may lead to better properties after irradiation. Furthermore, additions of minor concentrations of alloying elements, such as B, Al, Ti, and Zr have been suggested to strengthen the grain boundaries. New dilute Mo-alloys are being fabricated for testing.

Short rodlets with Mo and Mo-ODS cladding and 4% enriched fuel pellets have been under preparation for

irradiation in the ATR beginning in 2016. Additional irradiation in the Halden Reactor has been under preparation to begin in 2016.

3 Summary on results to date and challenges ahead

This feasibility study of coated Mo-alloy cladding for accident tolerant fuel has demonstrated excellent corrosion in simulated LWR coolants and great oxidation properties in 1000 °C. The thin wall Mo tube has adequate mechanical strength and ductility, and further improvement in the diametral ductility is continuing to provide better resistance to pellet-to-cladding mechanical interaction. Fabrication of rodlets for irradiation is underway.

For commercial deployment, it may be necessary to fabricate the coated tubes via mechanical co-reduction, rather than relying on the PVD process, as the latter can be prohibitively expensive and challenging for quality control. A feasibility study on forming metallurgical bonding between the outer coating and the Mo-alloy via hot hydrostatic pressuring (Hipping), and subsequent mechanical co-reduction to produce coated Mo tubes has been underway. It is also necessary to incorporate fabrication process control to achieve optimized mechanical properties.

While the corrosion resistance of the coated cladding may be adequate, it is desirable to improve the corrosion resistance of the Mo tube to ensure full reliability of the cladding in the event of loss of the outer coating. To achieve this feature, Mo-alloys, primarily Nb-containing ones, are being studied.

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