Thermomechanical Characteristics of Mo for Accident Tolerance Fuel Cladding under Internal Pressure

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ABSTARCT: The thermomechanical characteristics of Mo tube specimens were investigated over the ranges of temperature at 350^{o}C-900^{o}C by pressurizing the internal surface of test tube with an argon gas till the failure of test tubes. Due to very rapid oxidation of Mo even at relatively low oxygen, a protective coating of Zr alloy or advanced steel alloys was produced by PVD on the outer surface of Mo tube, and the induction heat treatment was conducted at various temperatures to refine the grain structure in order to improve the fracture toughness of Mo tube.

The ductility of as-extruded thin wall Mo tube remains inadequate to be used as a LWR fuel cladding. It is clearly evident that the ductility of Mo was improved by the Zircaloy 2 coating formed by PVD that may result from the metallurgical bonding of Zircaloy 2 coating to the Mo substrate, while no benefit of FeCrAl coating on the Mo ductility was observed. It is thus suggested that the coating density/porosity may play an important role for affecting the mechanical property of Mo. In addition, the ductility of Mo can be improved significantly by an induction heat treatment at higher than 1500^{o}C, providing the rupture strength to be comparable to the Zircaloy strength at the given temperatures that may be mainly contributed by altering the microstructure and grain size of extruded thin wall Mo tube.

Keywords: Accident tolerance fuel cladding, Mo, protective coating, pressurized tube test

1. Introduction

Zirconium alloys have been used most extensively as fuel assembly materials for water-cooled reactors [1]. These alloys have low capture cross-sections for thermal neutrons, maintain good mechanical properties both during and after irradiation with fast neutrons, and resist corrosion. However, zirconium is susceptible to embrittlement by hydrogen when hydrides are formed. However, under accident conditions at Fukushima in 2011, where the reactor is heated up due to loss of coolant, Zr alloys will rapidly react with steam to produce large quantity of exothermal energy and hydrogen at temperatures greater than 700-800^{o}C. To enhance the LWR fuel cladding to a severe loss of coolant accident, accident tolerance fuel (ATF) cladding is essential to reduce hydrogen generation rate and extend time to initiation of fuel rod melting, which occurs at >2000^{o}C.

EPRI has proposed Mo or its alloys as an alternate ATF cladding material [2-3]. Mo and its alloy cladding will provide several advantages to current Zr alloys, such as Zircaloy or Zr-Nb alloys, because of its high melting point, excellent high temperature strength, low coefficient of thermal expansion, high thermal conductivity and ductility, resistance to irradiation-induced swelling and corrosion resistance in liquid metal coolants. However, above about 400^{o}C, Mo forms oxide that slowly vaporizes, causing gradual metal loss. Thus, in order to achieve the ability for enhancing the performance of Mo under accident conditions, a protective coating on Mo is essential for increasing the oxidation resistance under LWR conditions and at high temperatures and Zr alloy (Zircaloy 2) or advanced stainless steel (FeCrAl) coating formed by a physical vapor deposition (PVD) method on Mo has been successfully proven to provide a protective layer.

In LWR, the fuel cladding is under the external pressure by coolant and thus the inner surface of fuel cladding is physically in contact with fuel pellets. A comprehensive report has been published to summarize the creep or mechanical properties of the Zr cladding alloys [1]. Thermal expansion of pellets during power ramp, irradiation growth, or pellet swelling increases the pellet diameter that consequently generates internal pressure in the fuel cladding. Such an internal pressure causes the thin wall tube of the cladding to strain. Therefore, under the certain conditions, the differential pressure may cause severe deformation of cladding and, thus rupturing of the tube. For an example, under pellet-clad mechanical interaction (PCMI) conditions, the cladding may be stressed in the axial direction.

Thus, understanding the high temperature mechanical behavior of metals is useful in designing the desired environmental resistant systems. In order to comprehend the complete mechanical characteristics of Mo cladding tubes, their behaviors under various conditions, e.g., internal pressure and temperature are to be investigated. For this purpose, the pressurized tube test (PTT) under internal pressure was designed and conducted to establish the fundamental mechanical property of bare and coated Mo under various temperatures and pressures that is applicable for LWR.

2. Experimental Procedures

2.1. Preparation of Test Specimens

Mo tubes (9-10mm OD with ~0.2mm wall thickness) are made of (1) pure Mo formed by powder metallurgy (PM Mo), (2) pure Mo fabricated by low carbon arc cast (LCAC Mo), and (3) oxide dispersion-strengthened (ODS) Mo containing ~0.3% La_2O_3 (ML) and provided by Rhenium Alloy Inc. Figure 1 shows the cross-section view of SEM image for LCAC Mo tube, showing the wall thickness in ~0.2mm.

In order to retain the structural integrity of Mo during normal and accidental conditions, a protective coating that is known to be stable chemically and physically in normal nuclear environments is formed on the outer surface of the Mo tube by a physical vapor deposition (PVD). The coating materials are the bar of Zircaloy 2, Zircaloy 4, and FeCrAl (~5wt.% Al + ~23wt.% Cr in Fe balance). Figure 2 shows the SEM image of Zirclaoy 2, Zircaloy 4, and FeCrAl coating (~50μml thick) formed by PVD on Mo tubes [3]. A very dense coating layer of Zircaloy 2 and Zircaloy 4 was produced, while some porosity on FeCrAl coating. More progresses have been made on PVD coating processes to produce a dense-defect free FeCrAl coating. In addition, in order to improve the mechanical property of Mo, the induction heat treatment (IHT) was conducted at the ranges of temperatures (1200°C – 1700°C) for various times (5 – 60 seconds). As an example, the microstructures of ML tubes before and after IHT at 1700°C are shown in Figures 3 and 4, respectively. It is clearly seen that the IHT process at 1700°C produced relatively more formation/distribution of uniform grain size [4].

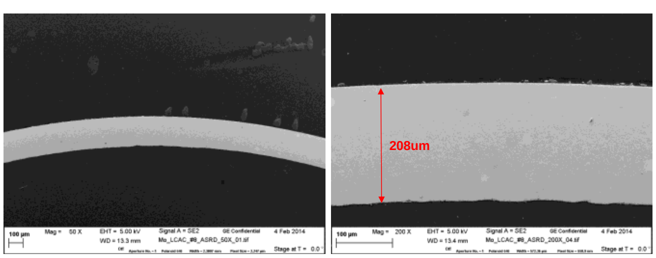

Figure 1: LCAC Mo tube (~8mil wall thickness)

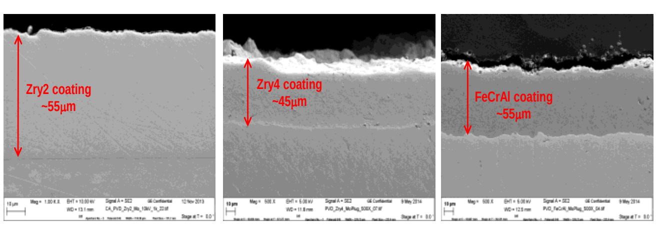

Figure 2: Microstructures of Zircaloy 2 and FeCrAl coating formed by PVD on Mo.

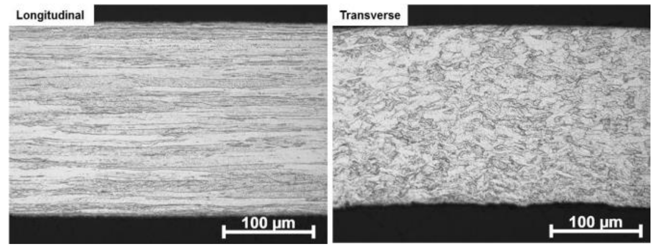

Figure 3: Microstructure of ML tube before induction heat treatment

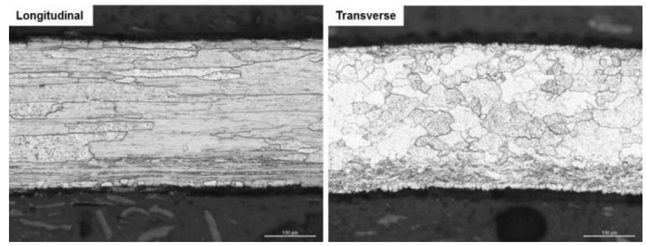

Figure 4: Microstructure of ML tube after induction heat treatment for 5 seconds at 1700°C

2.2. Pressurized Tube Test System

The pressurized tube test (PTT) system was designed to characterize the mechanical properties of thin wall Mo tubes with and without a protective coating for measuring the engineering strength and ductility under various temperatures. It consists of a custom made furnace and retort with quartz viewing windows in conjunction with a Keyence Model LS-7600 LED/CCD optimal micrometer to monitor in-situ displacement of test specimen by measuring continuously the diametral change of the tube. During the testing, the internal pressure, diameter micrometer, temperature and time is recorded electronically, and the rupture strength and diametral strain was calculated. The acquired pressure-displacement data were imported into the Excel files to plot the strain-stress curves.

After installing the test tube in the PTT system line, all system lines are first vacuumed and followed by purging in and out an Ar gas several times to remove an air in the test tube and system at room temperature before heating the furnace. A thermocouple is placed at the center of test tube specimen for monitoring the test temperature. After reaching the desired test temperature, an argon gas is then slowly introduced to the test tube in ~5psi interval every second. There were no holding times at any pressures. The displacement of outer diameter is monitored in-situ by a laser scan micrometer. The PTT facility at GEGRC is shown in Figure 5. This PTT system is capable of pressurizing it up to a 5,000 psi of argon gas within the internal surface of test tubes, operating upwards of 1000°C.

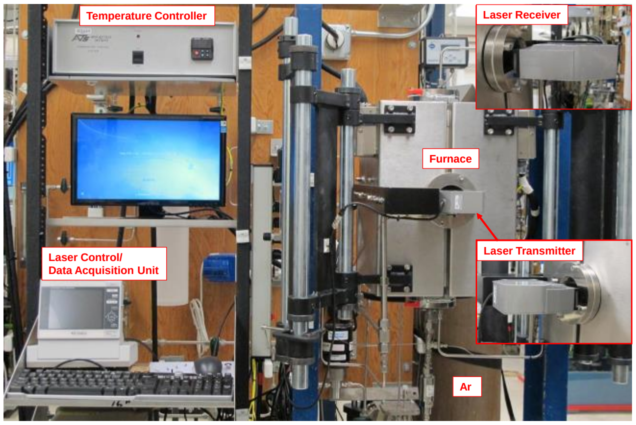

Figure 5: High temperature PTT facility at GEGRC.

3. Results and Discussions

3.1. Basic Equations for Calculation of Stress & Strain

It is well described that exposure of a thin walled tube to high temperature and high internal pressure causes the tube to strain. Under the proper conditions, the internal high pressure may cause severe deformation and eventually rupturing of the tube. Thus, it is very critical to understand the rupture strain behavior of a thin wall tube subjected to high temperature water or hypothetical loss-of-coolant accident (LOCA) in a water cooled reactor. In order to measure the rupture strain and stress, an incremental pressure at 1 psi/second was applied to a thin wall Mo tube with and without protective coating at a given temperature till the failure of test specimen was reached.

When a thin-walled tube or cylinder is subjected to internal pressure, a hoop or circumferential stress can be calculated in the thin wall as;

$$\sigma = \frac{pd}{2t} \qquad (1)$$

where σ = stress (MPa or psi)
p = internal pressure in the tube (MPa or psi)
d = original internal diameter, ID, of tube (mm or inch)
t = wall thickness of tube (mm or inch)

And, a diametral strain of a thin-walled tube was estimated as:

$$\varepsilon = \frac{(d_t - d_o)}{d_o} \times 100 \qquad (2)$$

where ε = diametral strain (%)
d_t = internal diameter of tube (mm or inch) at a given test time
d_o = original internal diameter of tube (mm or inch)

3.2. Stress-Strain Behavior of Zircaloy 2 Cladding and Mo

During a loss-of-coolant accident (LOCA) or an extreme condition at high temperature, the reactor coolant pressure may drop below the internal fuel rod gas pressure causing the fuel cladding to swell an, under some condition, rupture. Core behavior during a LOCA would depend on the type of accident, the time at which swelling and rupture occurred, the magnitude of ballooning (swelling), and the resulting coolant flow blockage. The degree of swelling and incident of rupture can be varied by various factors, such as cladding temperature, oxidation rate, hydrogen generation, etc. under the given condition.

The rupture behavior of Zircaloy 2 cladding depends on test conditions and various environmental conditions, for example, the hydrogen embrittlement, the presence of aggressive fission products, the localized strain, variations in the Zr oxide layer, etc. The pressurized tube test was conducted to measure the stress-strain properties of Zircaloy 2 cladding at various temperatures. Figure 6 shows the effect of test temperature on the stress-strain curves of Zircaloy 2 cladding, indicating the temperature dependence of the strength and ductility. A typical example of ballooned Zircaloy 2 cladding is also shown. This result is in a good agreement with literature [5].

The pressurized tube test was also performed to measure the strength and ductility of LCAC Mo at various temperatures. As shown in Figure 7, the diametral strain of LCAC Mo increases but its strength decreases, as the temperature increases. By comparing Figures 6 and 7, it is seen that the strength of LCAC Mo is much higher than that of Zircaloy 2 at a given temperature, but much lower ductility of LCAC Mo over Zircaloy 2. Photographs of ruptured test tubes are also shown in Figure 7. This low ductility may be contributed by the inadequate microstructure and high residual stress of Mo tube that resulted from the manufacturing process of extruded thin Mo tube. . In order to reduce the residual stress and to optimize the microstructure of a thin wall Mo tube, the development of post heat treatment is in progress and some preliminary data is followed.

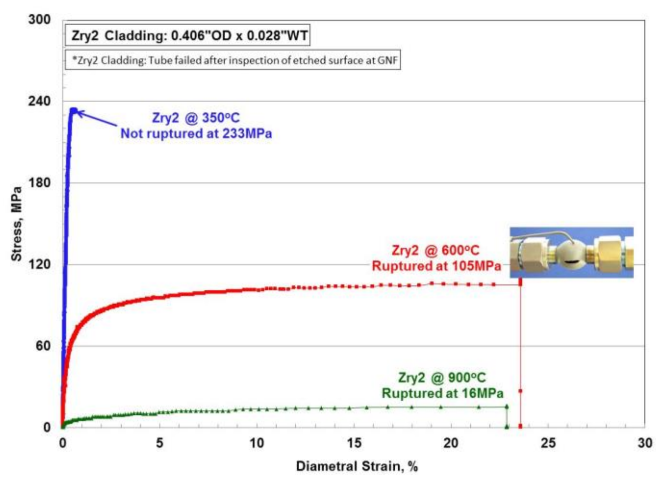

Figure 6: Engineering strain-stress curves for Zircaloy 2 cladding tested at three different temperatures.

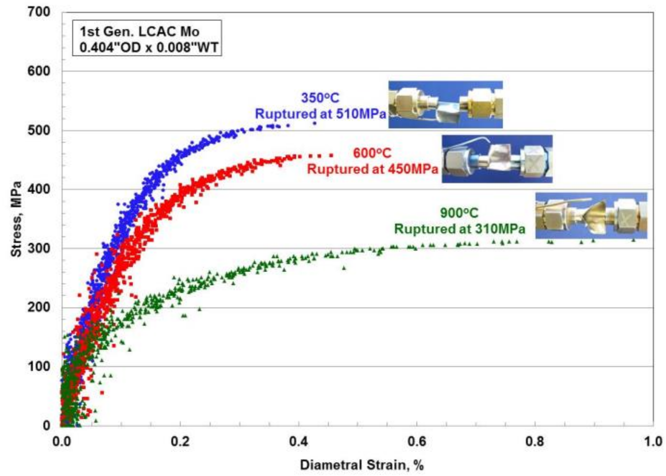

Figure 7: Engineering strain-stress curves of LCAC Mo tested at three different temperatures.

3.3. Effect of Protective Coatings on Stress-Strain Behavior of Mo

As stated above, two different types of protective coatings on the outer surface of Mo tube were deposited by PVD and the PTT was conducted to evaluate the effect of such coatings on the mechanical property of Mo. Figure 8 shows the stress-strain curve of bare LCAC Mo tube and coated PM Mo tubes at 350^{o}C and 900^{o}C. Photographs of ruptured test tubes are also included in a figure. It is evident that the Zircaloy 2 coating significantly enhances the ductility of Mo, but the FeCrAl coating does not; actually decreases it slightly. This different characteristic of Zircaloy 2 and FeCrAl coatings on the Mo ductility may be attributed by the degree of coating density (see Figure 2); a dense Zircaloy 2 coating and a less dense FeCrAl coating by PVD. It is thus suggested that the coating density/porosity may play an important role for affecting the mechanical property of Mo. In addition, the formation of metallurgical interdiffusional layer at the coating/Mo interface may improve the ductility of Mo [3]. More tests for understanding the mechanism of two different coatings and development of a denser FeCrAl coating process by PVD are in progress.

In addition, it has been well stated that PVD coatings have considerable residual compressive stresses that are caused by a thermal and structural mechanism [6]. Coating residual stresses may improve the performance of coated components and compressive stresses in PVD coatings may be desirable to enhance the mechanical properties of the substrate-coating interface and eventually prevent the premature failure. The internal stresses combine the intrinsic stress, resulting from the growth process and the thermal stresses from a mismatch in thermal expansion coefficient (TEC) between the coating and the substrate. Thus, similar ranges of TEC values between Zr (5.7ppm) in Zircaloy coating and Mo (4.8ppm) may improve the strain behavior, while a significant difference between Fe (11.8ppm) in FeCrAl coating and Mo may not. TEC values of each element were taken from literature [7].

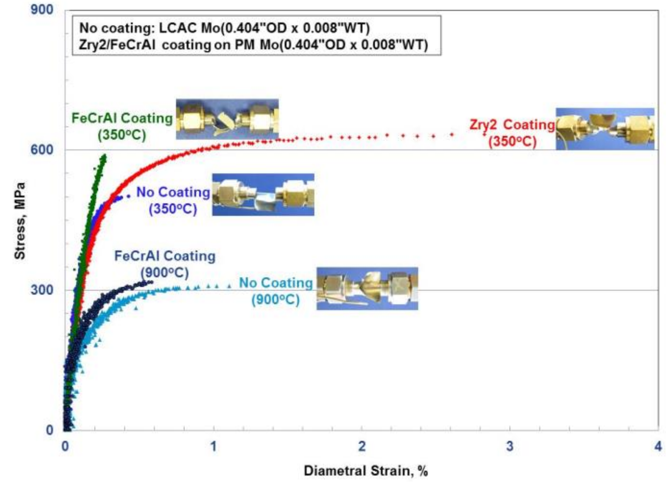

Figure 8: Effect of Zircaloy 2 and FeCrAl coatings on diametral strain-stress curves of LCAC Mo.

3.4. Effect of Induction Heat Treatment on Stress-Strain Behavior of Bare Mo

Induction heat treatment (IHT) is being applied to various conductive materials to relieve internal/residual stresses and refine the grain structure in order to maintain/increase the physical stability and fracture toughness of metals. Thus, IHT was conducted on extruded thin wall Mo tubes at 1200^{o}C-1700^{o}C for various times. The stress- strain behavior of IHT Ml tubes is shown in Figure 9 and summarized in Figure 10. It was observed that the rupture stress decreases with the increase of IHT temperature, while the strain increase as the IHT temperature increases.

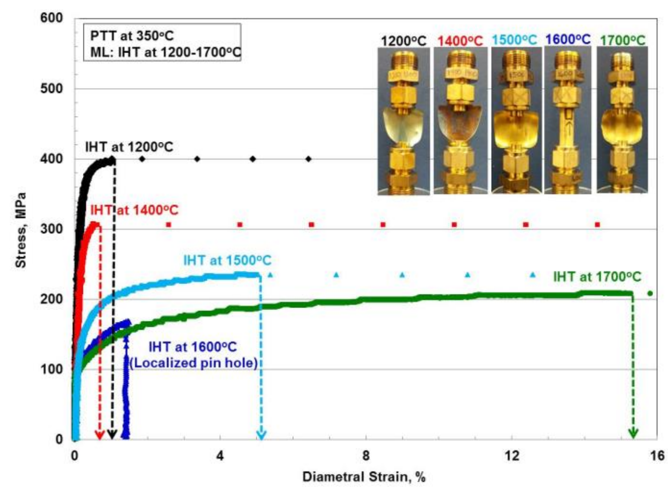

Figure 9: Effect of induction heat treatment at various temperatures on engineering strain-stress curves of ML.

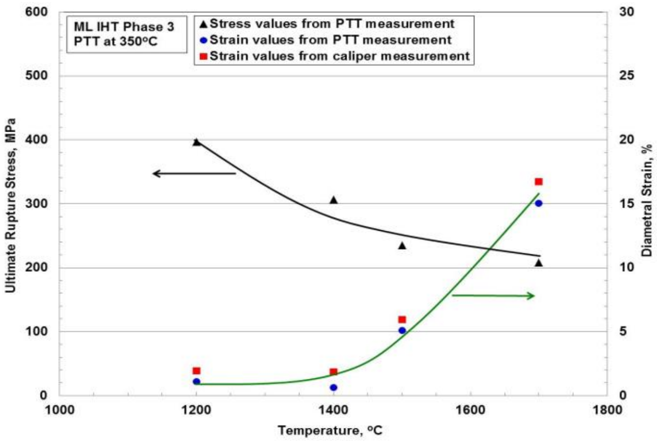

Figure 10: Effect of IHT temperature on rupture stress and diametral strain of ML tube.

By comparing the rupture stress of ML tube with that of Zircaloy 2 [5], the PTT result suggests that the IHT at 1600°C may produce the microstructure and grain size to be beneficial for enhancing the mechanical property of Mo for LWR application, but more tests are needed to develop the optimum IHT conditions. It has been reported that the refined microstructure of oxide dispersion-strengthened (ODS) with an addition of La_2O_3 for optimizing the grain size improved the strength and ductility, significantly [8] and the adequate heat treatment significantly influenced the fracture toughness of materials [9]. After the PTT, the fractured longitudinal surface modes were examined by SEM and their fracture images are illustrated in Figure 11. The cleavage fracture mode of ML heat treated at 1700°C was clearly shown, while the elongated intergranular fracture morphology on non-heat treated ML tube. Thus, the adequate heat treatment is necessary to increase the fracture resistance of thin wall Mo tubes and an optimization of IHT processes is in progress.

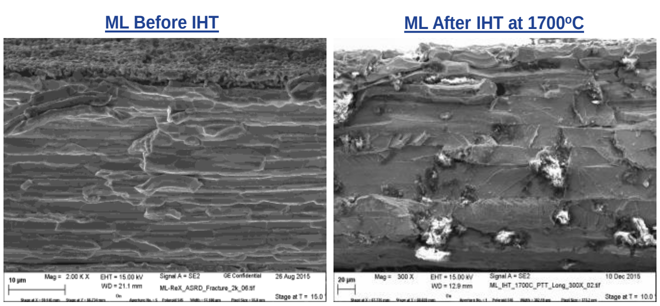

Figure 11: Longitudinal fracture morphology of ML before and after induction heat treatment at 1700°C.

4. Conclusion

The thermomechanical characteristics of thin wall Mo tubes (0.2mm wall thickness) with and without protective coatings formed by PVD were investigated at 350°C-900°C by pressurizing the internal surface of test tube with an argon gas. It was observed that the ductility of as-extruded thin wall Mo tube remains inadequate and needs to be improved for using as a LWR fuel cladding. It is interesting to note that the Zircaloy 2 coating enhances the ductility of Mo significantly that may be attributed by the metallurgical bonding and compressive stresses formed by the PVD process at the coating/Mo interface. However, no benefit with the FeCrAl coating was measured. This discrepancy between Zircaloy 2 and FeCrAl coatings may be explained by the microstructure of coatings; a dense Zircaloy 2 coating and a less dense FeCrAl coating. It is thus suggested that the coating density/porosity may play an important role for affecting the mechanical property of Mo. In addition, the ductility of Mo was improved significantly by IHT at 1500°C – 1700°C that may be mainly contributed by the change of microstructure and grain size. Based on the PTT results, the optimum heat treatment process is further under development for improving the structural longevity of Mo under LWR and severe accident conditions.

Acknowledgement

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