Journal of Nuclear Materials 448 (2014) 441–447

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

High temperature oxidation of molybdenum in water vapor environments

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ARTICLE INFO

Article history:
Available online 30 October 2013

ABSTRACT

Molybdenum has recently gained attention as a candidate cladding material for use in light water reactors. Its excellent high temperature mechanical properties and stability under irradiation suggest that it could offer benefits to performance under a wide range of reactor conditions, but little is known about its oxidation behavior in water vapor containing atmospheres. The current study was undertaken to elucidate the oxidation behavior of molybdenum in water vapor environments to 1200 °C in order to provide an initial assessment of its feasibility as a light water reactor cladding. Initial observations indicate that at temperatures below 1000 °C, the kinetics of mass loss in water vapor would not be detrimental to cladding integrity during an off-normal event. Above 1000 °C, degradation is more rapid but remains slower than observed for optimized zirconium cladding alloys. The effect of hydrogen–water vapor and oxygen–water vapor mixtures on material loss was also explored at elevated temperatures. Parts-per-million levels of either hydrogen or oxygen will minimally impact performance, but hydrogen contents in excess of 1000 ppm were observed to limit volatilization at 1000 °C.

1. Introduction

Development of new light water reactor (LWR) cladding variants that possess enhanced resistance to oxidation during off-normal conditions has gained attention following the events at Fukushima in 2011. A range of concepts have been proposed, including coatings for traditional zirconium-based cladding alloys, thin walled ferritic alloys constructed around the iron–chromium–aluminum (FeCrAl) system, or more non-traditional cladding materials such as silicon carbide. Each of these systems possesses varying degrees of attractiveness, as well as challenges to deployment, when judged from the perspective of industry. Enhanced resistance to oxidation under conditions representative of a loss of coolant accident (LOCA) has driven the advocacy of many of these proposals. The specific reactor type, accident scenario, and candidate fuel-cladding system dictate the details of the anticipated LOCA conditions [1,2]. In general, the oxidation resistance of a candidate cladding system is experimentally judged according to its performance at temperatures from 1000 to 1500 °C under atmospheres containing predominantly steam with minor partial pressures of hydrogen, oxygen, or nitrogen to simulate the coolant chemistries of specific reactors [3,4].

Resistance to high temperature oxidation in steam environments is only one of many key material performance challenges placed upon a successful LWR cladding material [5]. Qualification of a next-generation LWR cladding system that exhibits superior oxidation resistance to the thermochemical conditions anticipated of a LOCA would represent a meaningful advancement to the field. Yet the cost incurred by vendors and operators in development and deployment of a new cladding must be matched by performance gains if it is to see broad implementation.

Two broad avenues exist through which enhancements to LWR cladding can positively affect normal operation. Improvements offered in the following areas to augment improved oxidation resistance at elevated temperatures would greatly improve the business case justifying the time and expense necessary to develop, license, and deploy any new cladding technology. First, any means by which fuel failures, i.e. a breach of cladding during operation that results in the release of fission products into the coolant, could be reduced would be attractive. However, the improvements made by industry in this area over the past few decades leave little margin for significant gains. Secondly, performance enhancements that facilitate fuel operation to higher burnup could justify investment through reduction to future operating costs. Currently, oxidation and hydriding of conventional zirconium alloys serve to limit their service life by degrading the mechanical properties of the cladding, giving rise to both severe deformation and an increase in fuel failures. Materials or alloys that avoid these mechanisms

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http://dx.doi.org/10.1016/j.jnucmat.2013.10.043

of degradation could serve as a pathway to extended fuel cycles, reducing operator refueling downtime.

Molybdenum is one such candidate for a next-generation cladding material that could offer benefits across multiple areas relevant to LWR performance to high burnup. Foremost, it exhibits superior creep resistance and retains significant mechanical strength at temperatures above 1500 °C [6] owing to its high melt point (2600 °C). More importantly, it retains acceptable properties under neutron irradiation [7], although the majority of existing data has been collected under irradiation conditions relevant to fast reactor and fusion applications. Embrittlement following low temperature irradiation and the resulting increase in the ductile-to-brittle transition temperature (DBTT) has been a historic concern in use of molybdenum in irradiation environments [8], but recent studies have identified means of restricting this degradation through refinement of grain size or use of nanostructure oxide inclusions [9]. The thermal neutron cross section of molybdenum is higher than that of zirconium, but the penalty to neutron economy could be partially overcome through a reduction in the cladding thickness facilitated by its enhanced mechanical properties. Demonstration of thin walled molybdenum tubing capable of a maintaining fully hermetic seal around the fuel would require development and qualification of suitable fabrication and joining techniques, and is presently under investigation.

Many of the above benefits can be directly related to hypothesized performance at high burnup, predominantly with respect to wear resistance relevant to grid-to-rod fretting and retention of strength and resistance to deformation following prolonged exposure to elevated temperatures. However, the oxidation resistance of molybdenum is unknown under the thermochemical stimuli expected during steady state and possible transient reactor operations. Successful service as reactor cladding requires prolonged exposure to pressurized water at temperatures below 400 °C. Evaluation of the potential offered by molybdenum when judged by accident tolerant metrics requires consideration of its response to water vapor and hydrogen at temperatures in excess of 1000 °C. Performance when subjected to oxygen rich atmospheres is also relevant when considering a possible core breach, off-normal condition during transportation, or eventual used fuel storage.

This study was undertaken to explore the performance of molybdenum under both normal operating conditions and prototypic of those expected during a LOCA and station blackout. Molybdenum has long been anecdotally known to suffer aggressive material loss during exposure to oxygen at high temperatures, but few studies have investigated its performance in derivative oxidizing environments. The primary goal of this work was thus to explore the degree to which historic observations made in oxygen-rich atmospheres translate to water vapor and water vapor/hydrogen environments, and interpret these findings with respect to the potential of molybdenum or its alloys as an LWR cladding material.

2. Review of oxidation performance of molybdenum

Previous investigations executed to elucidate the oxidation behavior of molybdenum were prompted by exploration of its suitability for aerospace applications. These results conclusively demonstrated exceedingly poor oxidation performance. Aside from the occasional fundamental examination, oxidation of molybdenum has received minimal further interest. It is worth noting that the oxidation of molybdenum disilicide ($MoSi_2$) has received extensive attention given its excellent resistance to high temperature oxidation [10]. A functionally-graded cladding that takes advantage of the toughness and mechanical properties of molybdenum metal or one of its alloys but features a $MoSi_2$ outer coating for high temperature oxidation performance may be a system that warrants future investigation but is not the focus of the current study.

The few studies that have explored the oxidation of molybdenum in oxygen identify four critical temperature regimes of oxidation [11,12]. Below 450 °C, an adherent passivating oxide forms. The temperature range of 500–700 °C marks the transition region. Depending upon the partial pressure of oxygen available to the system, volatilization of MoO_3 may or may not dominate system response. MoO_3 possesses a vapor pressure of 6.08×10^{-6} atm at 600 °C, which increases to 4.69×10^{-4} atm at 700 °C [13]. Molybdenum trioxide then melts at just below 800 °C and boils at roughly 1150 °C [13]. The point at which MoO_3 liquefies upon formation marks the beginning of the third regime, which extends to the point at which the oxidation of molybdenum will immediately form a volatile species above 1150 °C.

Experimentally, the above regimes are typically manifested as only two distinct regions. Weight gain is generally observed at a rate that can be approximated through a parabolic fit at temperatures below 600 °C. Conversely, conditions above 700 °C are found to result in sample weight loss. The rate of mass loss increases drastically with temperature due to the transition from solid to liquid MoO_3 above 800 °C. Oxidation studies at conditions performed above this point in oxygen containing environments report that material loss occurs at a rate that is directly proportional to the availability of oxygen to the molybdenum surface [12]. For example, literature values for material loss due to oxidation at 1000 °C in an oxygen partial pressure of 0.1 atm approach 2 mg/cm^2 s [11].

The above results seem to suggest that molybdenum would perform poorly as a reactor cladding material. However, the critical unknown is how the kinetics exhibited during oxidation in severely oxidizing environments translate to those relevant to a LOCA. The fundamental physical properties of the system will remain unchanged; volatilization of MoO_3 is anticipated to dominate the response, and exposure to conditions above its melting point is likely to greatly affect system response. However, the degree to which oxidation of molybdenum in water vapor compares to previous observations carried out in air will dictate whether molybdenum can be considered a candidate accident tolerant cladding.

3. Experimental procedure

Two separate experimental methods were used in the current study. First, autoclave testing was performed in order to assess the stability of molybdenum in prototypic BWR (boiling water reactor) or PWR (pressurized water reactor) coolant chemistries at standard operating conditions over extended time intervals. Second, thermogravimetric analysis (TGA) was used to explore the response of molybdenum to 100% H_2O as well as H_2O–O_2 and H_2O–H_2 mixtures at temperatures up to 1200 °C for up to 4 h time intervals. This test was designed to study the response of molybdenum to conditions representative of those that an LWR cladding would be exposed to during a LOCA. The specific procedures used for each test are outlined below.

3.1. Autoclave testing

A high temperature-high pressure autoclave was used for evaluating the corrosion rate of molybdenum under representative reactor operating conditions. Specimens of pure molybdenum tubes (12.7 mm diameter, 12.7 mm height, 0.76 mm wall thickness) were polished on all surfaces using 600-grit emery paper lubricated with water. All test specimens were then rinsed ultrasonically with high purity water and weighed prior to insertion.

The testing system consisted of a one liter stainless steel autoclave, a heat exchanger, a high pressure pump (Model 7120, Lapp Pulsafeeder, Rochester, New York), and a conditioning glass column for controlling water chemistry. Water in the loop was purified through a demineralizer, an organic removal column, and a sub-micron filter before passing into a 3.78 L conditioning column. The water was equilibrated with appropriate mixtures of nitrogen, oxygen, and hydrogen to establish the desired water chemistry. Oxygen (FAM Oxytrace, Swan Analytical Instruments, Wheeling, Illinois) and hydrogen (Orbisphere 26322, Hach, Loveland, Colorado) monitors were used for measuring the dissolved gas content in the inlet and outlet streams.

Tests were performed in simulated BWR water chemistry containing 1.0 part-per-million (ppm) O_2 (BWR–NWC) or 0.3 ppm H_2 (BWR–HWC) at 290 °C, and in a simulated PWR primary water chemistry containing 3.5 ppm H_2 at 330 °C. A refreshed high purity water loop ensured controlled chemistry and H_2 fugacity during testing.

3.2. Thermogravimetric testing

Molybdenum sheet (Eagle Alloys, 99.9%) was used in the current study for TGA testing. The 0.25 mm molybdenum sheet was sectioned into rectangles nominally 5 × 15 mm in size. Measurement of the precise surface area of each sample was performed prior to testing by measuring each edge using a digital micrometer with an error of ±0.1 mm. The samples were then immersed in acetone and then cleaned using methanol and lint-free wipes. The initial mass of each sample was obtained using a balance (XP205, Mettler-Toledo, Columbus, Ohio) calibrated to ±0.1 mg.

Thermogravimetric analysis was performed using a specially configured commercial instrument (STA 449 F3, Netzsch Instruments, Selb, Germany) coupled with a water vapor generator and gas mixing system used to obtain the desired thermochemical testing condition. The protective tube, sample holder, and all other fixturing inside the TGA were alumina. The sample temperature was monitored using a Type-S thermocouple located directly beneath the sample platform. The water vapor delivery lines and all fixturing in the TGA were maintained above 200 °C at all times using backing heaters to avoid complications induced by adsorption of water on internal surfaces. The sample chamber was evacuated and backfilled a total of three times to limit the impact of atmospheric oxygen on the measured oxidation. The final of the three steps utilized a turbo pump to obtain pressures below 10^{-3} mbar. Argon passed through a copper oxygen getter (2A, Centorr Vacuum Industries, Nashua, New Hampshire) was used to backfill the chamber after each evacuation as well as to surround the sample during heating to the test temperature. An inline zirconia oxygen sensor (RapidOx OEM447, Cambridge Sensotec, St. Ives, United Kingdom) was used to monitor the oxygen content in the gas being delivered to the sample chamber as well as to verify the stability of the water vapor mixtures being delivered to the sample. The gettered argon maintained an oxygen partial pressure below 10^{-15} ppm for all experiments performed here.

Four sample atmospheres were used in the current study. First, oxidation studies were performed in synthetic air (20% oxygen carried in argon), chosen to provide a comparison to the limited data available in the literature. The synthetic air mixture used for this study was flowed at 200 mL/min during the isothermal test periods. Second, 100% water vapor[1] at atmospheric pressure using a high precision vapor generator (ASTEAM DV2MK, Bronkhorst High Tech Instruments, Ruurio, The Netherlands). Water vapor flowed at 5.26 g/h through a heated transfer line held at 200 °C before reaching the oxygen sensor and backing heater held at 600 °C. The vapor then passed through a series of alumina baffles maintained within 100 °C of the test temperature before reaching the sample chamber.

The two final thermochemical conditions produced for this study were oxygen and hydrogen-containing water vapor mixtures. Although it is likely that the majority of any oxygen present in a BWR coolant chemistry would be consumed by hydrogen generated by both the cladding as well as other in-core components during the early stages of a LOCA, understanding the effect of small quantities of oxygen on the oxidation of candidate cladding materials could be important in other off-normal scenarios. This is particularly true of molybdenum, where its performance in high-oxygen environments is poor. The gas mixing system used in conjunction with the water vapor generator was used to inject 1 ppm oxygen to the water vapor to explore this effect at select temperatures.

Three hydrogen/water vapor environments were generated in the same way to explore the opposite effect. The inclusion of small amounts of hydrogen is not only more representative of the coolant chemistry in certain reactors, but is also clearly the anticipated thermochemical evolution during a LOCA, as high temperature water vapor begins to oxidize in-core components to free hydrogen. Three separate hydrogen/water vapor mixtures were included in this study: 100, 1000, and 10,000 ppm H_2.

4. Results and discussion

4.1. Autoclave testing

The results of the autoclave testing are shown in Fig. 1. The effect of oxygen potential on the observed weight loss is readily apparent. The PWR water chemistry containing 3.57 ppm H_2 exhibits much slower weight loss than the 0.3 ppm H_2 BWR test. Finally, the oxygen-containing autoclave test revealed significant weight loss at one month of testing whereupon testing of this condition was discontinued.

A more detailed analysis with interrupted testing and characterization of the resulting microstructure is needed to fully ascribe precise mechanisms to the observed long-term behavior. However, it appears probable that dissolution of the base material is enabled through oxidation. The growth kinetics of the oxide would

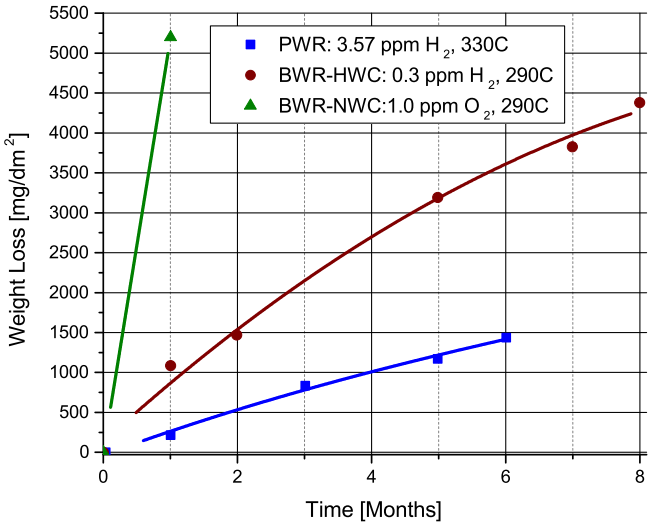

Fig. 1. Weight loss measured for molybdenum samples exposed to autoclave testing performed over several months.

[1] Due to the altitude of Los Alamos, 100% water vapor equates to a pressure of approximately 0.78 atm.

decrease as hydrogen is added to the system. The baseline performance of molybdenum under steady state operating conditions appears to be acceptable for short exposure periods for the two hydrogen-containing water chemistries studied here if judged only according to an ability to retain clad thickness. Long term service of pure molybdenum is still in question, as corrosion products could perturb coolant chemistry outside of acceptable limits.

4.2. Thermogravimetric analysis of molybdenum oxidation in synthetic air

Fig. 2 displays results for experiments performed at varying temperatures in a synthetic air environment. In this atmosphere, molybdenum displays primarily linear oxidation behavior below 650 °C. The data obtained below 650 °C exhibited good agreement with previous low temperature molybdenum oxidation studies [11]. In addition to the data plotted in Fig. 2, tests were executed at 400 °C. The weight change at 400 °C was within the error of the technique and as such is not shown. Extended testing consisting of oxidation executed over tens of hours is necessary to verify the oxidation kinetics at these lowest temperatures. Although not overly significant to reactor operation, resistance to oxidation in air at these temperatures must be fully understood in order to evaluate possible transportation and used fuel storage scenarios.

In the temperature range of approximately 650–750 °C, both oxidation of molybdenum to MoO_3 via the below reaction and volatilization of the MoO_3 occur simultaneously.

$$Mo + \frac{3}{2}O_2 \Rightarrow MoO_3 \quad (1)$$

The increasing importance of MoO_3 volatilization is evident in the positioning of the 650 °C weight gain curve below that observed at 600 °C. At 650 °C the oxidation kinetics still dominate compared to the volatilization rate, but the volatilization is significant enough to depress the overall weight gain. The curve obtained for 700 °C exhibits exhibits clear paralinear behavior. The kinetics are initially governed by oxidation of the molybdenum, exhibited by the weight gain in the first 30 min of the experiment. A steady state is then reached such that the combined effects of the species diffusion for additional oxide formation and MoO_3 loss due to volatilization equate to the overall weight loss rate measured.

Finally, the last two temperatures investigated at 800 °C and 1000 °C display extremely rapid weight loss, hypothesized to result from the formation of liquid MoO_3 with an accompanying increase in vapor pressure. Both the 800 °C and 1000 °C runs were terminated following establishment of a clear linear weight loss in order to avoid excessive volatilization within the sample chamber.

Bartlett executed an extensive investigation of the oxidation behavior of molybdenum above 1000 °C as a function of the supplied partial pressure of oxygen [12]. Above 1300 °C, molybdenum was lost at nearly 1 mm per hour even under the lowest oxygen partial pressure examined, a p_{O_2} of 10^{-6} atm. As the oxygen availability increases, Bartlett reports increasing loss rates up to a temperature of nearly 2000 °C. Above this temperature, the effect of p_{O_2} does not appear to increase loss above a p_{O_2} of 10^{-2} atm. Material loss under these conditions was observed to plateau at roughly 0.5 mm per minute. This response is not likely to be overly significant to service as LWR cladding, but it is important to understand that molybdenum will exhibit very high volatilization rates if exposed to oxidizing environments at high temperature.

4.3. Thermogravimetric analysis of oxidation in water vapor

The weight change measured for samples exposed to a 100% H_2O environment is plotted in Fig. 3 for temperatures ranging from 600 to 1200 °C. Measurements were again performed for temperatures of 400 and 500 °C, but no deviation outside the error of the instrument was observed following a four hour test. Extended testing performed over tens of hours would be necessary to evaluate the kinetics under these conditions.

The absolute weight loss values plotted in Fig. 3 are significantly lower than those plotted in Fig. 2. The oxidation kinetics of molybdenum is indeed significantly retarded when H_2O is the oxidizing medium, as opposed to oxygen. The reaction governing the oxidation involves the same metallic reactant and product. However, as oxidation must progress with water vapor, hydrogen is an additional product.

$$Mo + 3H_2O \Rightarrow MoO_3 + 3H_2 \quad (2)$$

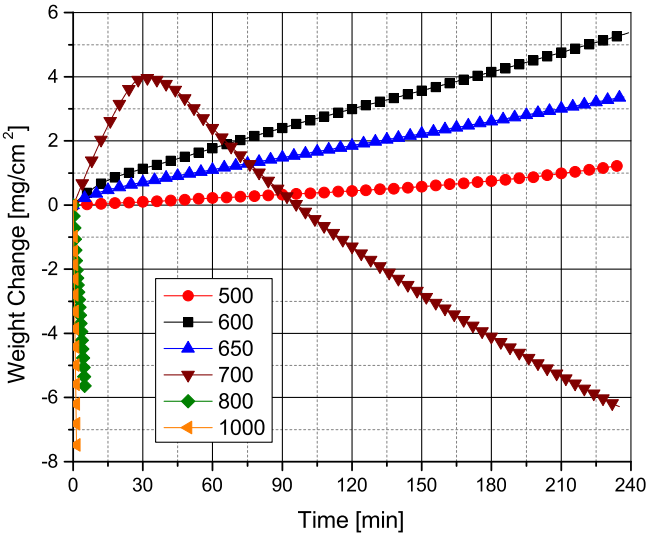

Fig. 2. Weight change measured for molybdenum samples exposed to synthetic air at a range of temperatures. Only a small fraction of data points for each temperature are plotted for clarity.

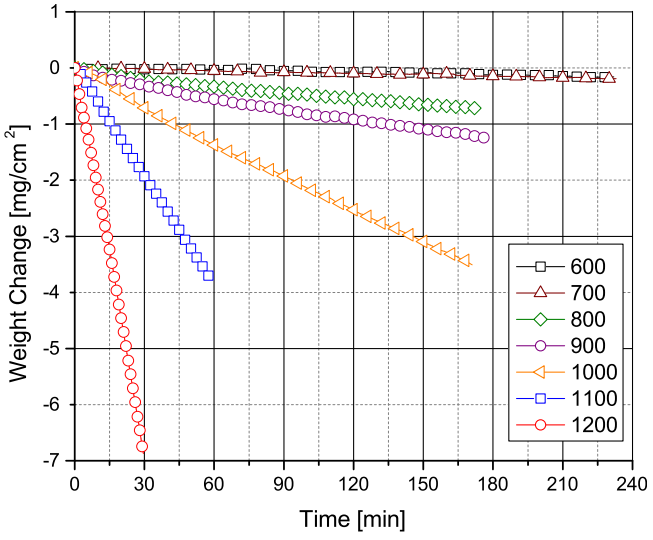

Fig. 3. Weight change measured for molybdenum samples exposed to 100% water vapor at a range of temperatures. Only a small fraction of data points for each temperature are plotted for clarity.

The production of hydrogen during steam oxidation of cladding has recognized importance to LOCA evolution. Examination of Eq. (2) reveals an additional concern that must be considered in discussion of the accident tolerance of molybdenum cladding. Conventional zirconium cladding alloys produce two moles of hydrogen per mole of zirconium consumed in formation of ZrO_2. This increases significantly in the oxidation of molybdenum; three moles of hydrogen are now produced per mole of molybdenum consumed in formation of MoO_3. The degree to which this is a concern is dictated by the rate of oxidation and the total quantity of material consumed. The drive to maintain neuronic performance would likely require that significantly less molybdenum is present in the core compared to the reference zirconium case; this could limit the concern posed by increased hydrogen production per mole of base material.

The effect of gas flow rate was also investigated in a preliminary manner. As discussed above, the rate of material loss is strongly dictated by the availability of oxygen during oxidation at very high temperatures. This effect in water vapor was probed by increasing the water vapor flow rate to roughly double that used for the full matrix. Temperatures from 700 to 1000 °C were investigated, and it was found that the loss rates increased significantly. The material loss rate measured at 700 °C increased from 0.04 to 0.30 μm/h, the rate measured at 800 °C increased from 0.20 to 0.80 μm/h, the rate measured at 900 °C increased from 0.40 to 1.1 μm/h, and the rate measured at 1000 °C increased from 1.2 to 2.7 μm/h. This suggests that a very strong pressure effect is present in the oxidation kinetics of molybdenum in water vapor.

It has been previously hypothesized that the kinetics of molybdenum oxidation in oxygen-rich environments are so rapid that localized oxygen depletion can occur [14]. However, this was attributed only to conditions where volatilization was extremely rapid such that the kinetics of the chemical reaction (Eq. (1)) is rate limiting, opposed to the transport of oxygen serving to dictate oxidation. This does not appear to agree with the observation here. Instead, the observed dependance of oxidation upon flow rate is greatest at 700 °C and decreases with temperature. The increasing volatilization rate measured as a function of temperature should drive the opposite response, increasing the importance of chemical kinetics on the observed oxidation. No conclusions can be drawn from the current experimental data. Further studies performed as a function of water vapor content, flow rate, and possibly specimen geometry are necessary to fully explore this observation.

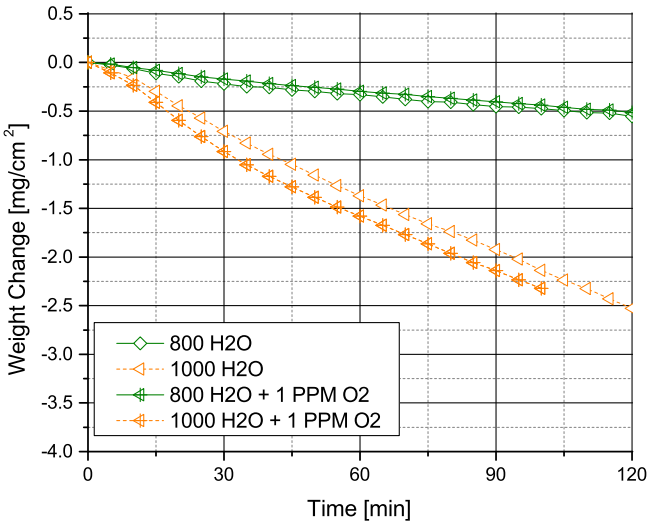

Fig. 4. Weight change measured for molybdenum samples exposed to water vapor and 1 ppm oxygen at 800 and 1000 °C. Only a small fraction of data points for each temperature are plotted for clarity.

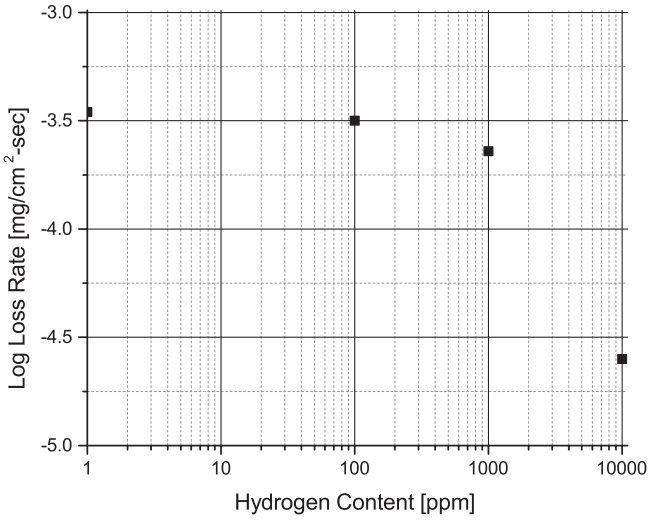

Fig. 5. Calculated material loss rates observed during testing at 1000 °C as a function of hydrogen content.

4.4. Effect of oxygen and hydrogen additions on kinetics of molybdenum oxidation in steam

The impact of oxygen additions on the oxidation of molybdenum under water vapor was not found to significantly alter the observations above. Fig. 4 highlights the effect of 1 ppm oxygen on the material loss measured for both 800 and 1000 °C. Both measurements performed with the additional oxygen do exhibit greater mass loss. This is more pronounced in the 1000 °C test. Material loss is observed to accelerate in the first 30 min of the test compared to the experiment conducted in pure water vapor. It is hypothesized that the addition of oxygen does facilitate a more rapid initial oxidation such that volatilization can more quickly reach its steady state rate. However, after 30 min material loss occurs at the same rate regardless of small amounts of oxygen present.

Fig. 5 highlights the results of testing performed to probe the effect of hydrogen content on oxidation. In addition to its presence in certain LWR coolants, hydrogen will undoubtedly be produced in significant quantities during a LOCA as oxidation of other in-core components progresses. Higgs et al. report that during a clad breach the H_2/H_2O ratio may reach as high as 0.1 during a LOCA [15]. Much of this is generated by oxidation of the zirconium cladding and as such this value would change in a hypothetical molybdenum-clad fuel. However, this work does provide a general indication of the hydrogen contents that could be relevant. The results of Fig. 5 illustrate the expected affect of hydrogen measured during oxidation at 1000 °C. The loss rate calculated for 100% water vapor alone does not change significantly with the addition of 100 ppm H_2, but 1000 ppm does begin to measurably reduce the material loss rate. Finally, 10,000 ppm H_2 significantly retards material loss. A comparison of the mass loss rate measured under this condition to the tests performed in pure water vapor reveals that volatilization has been limited to the magnitude observed below 800 °C.

Testing performed at 10,000 ppm H_2 did result in a different post-test appearance of the experimental apparatus compared to the other experiments executed in this work. Black deposits were found deposited on the alumina fixturing of the sample chamber surrounding the specimen. This contrasts with observations following all other experiments in conditions prone to MoO_3 volatilization. Yellowish anisotropic crystals generally were found

extending from the thermocouple stem and protective fixturing. A dark bluish coating was also observed at the extremes of the furnace hot zone. This observation led to the hypothesis that the H_2O-10,000 ppm H_2 test performed at 1000 °C produced local thermochemical potentials significantly different from all other conditions examined. It is probable that the reducing environment greatly limited transport of volatile MoO_3 within the test chamber. This effect could have important implications to the use of molybdenum as LWR cladding where redistribution of molybdenum via MoO_3 may be a significant concern relevant to LOCA performance.

4.5. Summary of volatilization rate and interpretation relevant to LWR cladding applications

The oxidation observed under all conditions included in this study rapidly converged to linear kinetics. Given the strong dependencies of oxidization rate constant on the available pressure of either oxygen or water vapor, a full kinetic development is not pursued in this initial study, The linear weight gain or weight loss observed at each temperature investigated in both synthetic air and water vapor is provided in Table 1. More importantly, this term is converted to a linear consumption rate through normalization using the density of molybdenum. This provides a rapid means to assess the impact of a prolonged thermochemical condition on the integrity of molybdenum cladding or other component.

Not surprisingly, oxidation in air at 1000 °C would result in near total consumption of a hypothetical LWR cladding geometry in a matter of hours. Examination of the rates observed for water vapor reveal that temperatures of over 1200 °C are needed to begin to degrade the cladding thickness at rates that are significant, even to thin-walled tubing variants. A 0.4 mm thick cladding could withstand nearly 4 h at 1200° before 10% of its initial cladding thickness is lost. In comparison, even the highest performing optimized zirconium cladding variants (e.g. M5, ZIRLO, E110) are nearly fully converted to ZrO_2 under these conditions [3] and would provide no mechanical integrity or barrier between the fuel and the reactor pressure vessel.

5. Conclusions and discussion of necessary future work

The oxidation and volatilization of molybdenum at elevated temperatures has been shown to be severely retarded in water vapor-containing atmospheres compared to that observed in strongly oxidizing atmospheres. Exploratory investigations of the effect of small additions of oxygen and hydrogen on this response have also shown that no detrimental effects should be expected at the high temperatures investigated here, but the corrosion rates of molybdenum under normal operating conditions suggests that either alloying or coating methods would be necessary to avoid unallowable fluctuations in coolant chemistry over several months. Exploration of potential molybdenum alloys or coating techniques capable of enhanced corrosion resistance is currently ongoing [16].

The volatilization rate of molybdenum determined for even the highest temperatures in water vapor included in this study would not result in a loss of cladding thickness over the course of tens-of-hours that would be the limiting factor in cladding integrity. However, conditions where the cladding temperature is maintained above 800 °C warrant further investigation as the presence of liquid MoO_3 may have implications beyond the potential loss of cladding thickness. The presence of significant amounts of MoO_3, or even a thin but semi-continuous wetting of the clad surface, could pose a concern through the formation of low melting point eutectics with other core components or disruption to coolable geometry. Preliminary investigation of the effect of water vapor pressure and flow rate suggest that a strong dependence exists and must be studied further.

The results of this work highlight that catastrophic oxidation and material loss through volatilization of MoO_3 is not a decisive issue in the exploration of the feasibility of molybdenum or molybdenum derivative as LWR cladding. A wide range of other fundamental material performance issues remain to be investigated, aside from the critical, but more challenging, validation of performance under LWR-relevant irradiation conditions. The effect of comparatively low levels of hydrogen on oxidation kinetics was included here. No indication of hydriding was observed, but this must be qualified in that the test times and temperatures of this study were limited. The solubility of hydrogen in molybdenum [17,18] is not as significant as found in zirconium [19], and limited investigations of the Mo-H binary system do not report the existence of any molybdenum hydrides [20]. However, investigations similar to those performed for zirconium cladding alloys [21] are necessary to further quantify this behavior.

The existence of multiple molybdenum-nitride phases is also reported [22]. The presence of nitrogen would occur during a full loss of containment, but is also relevant to certain variants of PWR failures [23]. Nitrogen is understood to significantly accelerate degradation of zirconium alloys as it degrades the structure of the oxide scale, thereby allowing more rapid oxidation of the base metal [24]. Nitrogen was intentionally excluded from the thermochemical matrix included here. The kinetics measured in this work obtained in synthetic air are less extreme than historic data obtained for 10% oxygen carried in nitrogen above 800 °C [11]. This could suggest that nitrogen may act as a catalyst, but the differences in experimental techniques used between the historic and current studies suggest a more detailed analysis is necessary to determine the effect of nitrogen. Even if a similar mechanism did translate to molybdenum, it is not clear how it would affect the oxidation observed here; the MoO_3 volatilization rate dominates system response at the majority of temperatures of relevance to LOCA analyzes.

Table 1
Tabulated mass change rates of molybdenum calculated based upon the linear oxidation or volatilization regime that dominates each temperatures and condition. These loss rates are then converted to a material consumption rate in the final columns for the conditions where volatilization is observed.

Temperature (C)	Mass change (mg cm^{-2} s^{-1})		Consumption rate (μm h^{-1})	
	20% Oxygen	Water vapor	20% Oxygen	Water vapor
500	+6.0E−5			
600	+3.4E−4	+1.3E−5		
650	+2.0E−4			
700	−8.4E−4	−1.2E−5	2.9	0.04
800	−1.9E−2	−6.3E−5	67	0.20
900		−1.1E−4		0.40
1000	−8.9E−2	−3.5E−4	310	1.2
1100		−1.1E−3		3.7
1200		−3.8E−3		13

Acknowledgements

Portions of this work were supported by the U.S. Department of Energy, Office of Nuclear Energy Fuel Cycle Research and Development program. Autoclave corrosion testing has been funded by the Electric Power Research Institute. E.A. Sooby would like to express appreciation to the Seaborg Institute at Los Alamos for supporting her work on this project.

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