Numerical and experimental investigation of high temperature steam oxidation of molybdenum cladding specimens applied to accident tolerant fuel

S S Bazyuk, Yu A Kuzma-Kichta, N Ya Parshin, K K Polunin, and D M Soldatkin
FSUE “SRI SIA “LUCH”, Zheleznodorozhnaya 24, Podolsk, 142103, Russia
bazukss@sialuch.ru

Abstract. The results of high temperature steam oxidation tests of cladding specimens made of VCPM at nominal test temperature of 1200 °C and exposure duration of up to 8.5 hours at GASPAR facility are presented. The experimental data were obtained by the steam-molybdenum reaction rate constant in the range of steam mass rates from 10 to 120 mg/s and compared with the calculation results of oxidation process taking into consideration the kinetic and diffusion mechanism.

1. Introduction
Nuclear technology and safety enhancements are the terms to steady development of nuclear industry. After Fukushima Dai-Ichii disaster has happened, new structures, nuclear fuels and rod claddings for accident tolerant LWR are being developed all over the world under design basis accident (DBA) and beyond design accident (BDA). To prevent steam-zirconium reaction new modifications of regular rod claddings are being studied as well as the option of structural change (FeCrAl steels [1], SiC ceramics [2], and refractory molybdenum [3]). Long-term ATF modifications are supposed to UO2 pellets replacement to high dense, thermal conductive and refractory fuel compositions (UN, U3Si2, UZrCN) [4]. The prospect structural material for tolerant rod claddings is molybdenum and its alloys due to high melting point (2620 °C), thermal conductivity (~ 110 W/(m·K)) and fatigue strength (~ 320 MPa) whereas the fission cross section of thermal neutrons (2.1 barn) [5, 6] is quite low. However the high-temperature (HT) Mo oxidation kinetics in water steam has been little studied and Mo quenching under reflooding conditions during Loss of Coolant Accident (LOCA) has not been previously investigated.

The PWR and WWER reactor facilities fabricated with both zirconium and tolerant fuel rods cores must keep safety in nominal and accident conditions. Heat-up and quenching performance of fuel rods for exploited and advanced LWR under LOCA are determined by heat transfer to two-phase flow, core structural degradation including HT steam oxidation of rod claddings. For example, molybdenum trioxide under atmospheric pressure and temperature above 500°C starts to volatilize and close to MoO3 melting temperature (TmMoO3 = 801 °C) the volatilization rate becomes equal to its formation rate [8].

The reaction rate constant, steam-molybdenum reaction (SMR) heat effect with hydrogen generation at atmospheric pressure and temperature above 1200°C have not been enough studied till nowadays [9, 10]. In papers [11, 12] the experimental data on reaction rate constant and SMR heat effect of rod cladding specimen made of pure vacuum-melted molybdenum (VCPM) up to 1470°C
were studied. However the performed investigation was carried out at fixed steam mass rate.

In this paper the results of flow parameters influence on high temperature steam oxidation characteristics of tolerant rod VCPM cladding specimens at temperatures about 1200 °C and individual exposure duration longer than 3 hours (8.5 hours in total) are presented.

2. The description of studied cladding specimens and GASPAR facility

The specimens with nominal dimensions of 11.7x6.7x4.5 mm (Dx dx L) were prepared by fragments cutting out of initial tube. Chemical composition of VCPM specimens consisted of 99.92 mass % of Mo, impurities of 0.005 % O and N and less than 0.03 % C. To relieve stresses forming under electric erosion cutting the cladding specimens were processed thermally at the temperature of 1100°C in argon medium at 10⁻⁴ mmHg during 1 hour. The measurements of initial density and outer surface roughness showed values of 10.17 g/cm³ and Ra2.5, respectively. Exact orientation of cladding specimen during post-test results analysis was achieved by specimens 1 mm wide wall cut-off by electric erosion method. To optimize the rod quality, the triple use of single cladding specimen was used three times.

High temperature interaction of VCPM rod cladding specimens with steam oxidation was studied at GASPAR facility. The specimens were oxidized in ceramic tube Ø28x2 mounted in the furnace graphite heater. The experiment is preceded by a study of the initial state of cladding specimens and their weighing with an accuracy of 0.1 mg. The inner facility cavity is cleaned out of oxygen-containing mediums and air by the argon flow. Saturated steam with mass rate of (10 – 120) mg/s flows from the steam generator to the superheater; then, it is heated up to (900 – 1000)°C and passes to the high temperature zone of the furnace. The rod cladding specimens are oxidized at given temperature (900 – 1200) °C in steady state conditions at isothermal region of 60 mm length where temperature gradient does not exceed 0.5 K/mm. Then the rod cladding specimen is removed out of furnace and cooled down by the steam flow with the rate not less than 20 K/s. When HT oxidation is finished, the cladding specimens are weighed for the second time. The steam mass rate was given by voltage and current supplied to the steam generator and was measured by the mass method with the 600 s periodicity.

3 The results of thermogravimetric tests

The characteristic thermal regimes of VCPM cladding specimens steam oxidation at nominal test temperature of 1200°C and exposure time of 3 hours are presented in fig. 1. The overall duration of heat-up and cooling-down stages amounts to (17-33) % of exposure duration at nominal temperature. The intensity of cladding specimen oxidation defined as SMR rate constant was determined by the proposed calculation method of equivalent duration that took into consideration unsteady regimes.

The equivalent duration of cladding specimen oxidation was determined using measured temperature regimes. The comparison of experimental data obtained at various temperatures (the uncertainty range of TC readings is ± 20°C) and related to the given temperature $T_0$ was carried out in accordance with equivalent oxidation duration of cladding specimen oxidation evaluated by two ways.

According to the first method

$$\tau_{\text{eff}} = \frac{\tau_2 - \tau_1}{\int_{\tau_1}^{\tau_2} T_{\text{clad}}(\tau) d\tau / T_0}$$

where $T_{\text{clad}}$, $T_0$ are current temperature of rod cladding specimen and nominal test one (1200 °C), $\tau_1$, $\tau_2$ are time points, corresponding to the onset and end of specimen oxidation. Following the second method

$$\tau_{\text{eff}} = K_T \cdot (\tau_2 - \tau_1)$$
where $K_{\tau} = \frac{1}{\tau_2 - \tau_1} \int_{\tau_1}^{\tau_2} \exp\left[\frac{Q}{R T_{\text{clad}}(\tau)}\right] d\tau \int \exp\left(-\frac{Q}{RT_0}\right)$. $Q = 2.329 \cdot 10^5$ J/mole, $R = 8.314$ J/(mole·K).

For the calculation of $\tau_{\text{eff}1}$ and $\tau_{\text{eff}2}$ HT oxidation was assumed to occur as the specimen temperature exceeded 400 °C. In respect with the above-mentioned method the experimental data were obtained and presented in table 1 as well as processed results of dimension and mass changes of cladding specimens due to SMR. The maximal effective oxidation duration of cladding specimen in single test amounts to about 4.5 hours and the total one with repeated tests is about 8.5 hours.

### Table 1. Test regimes of VCPM cladding specimens during HT steam oxidation, change of specimen geometry characteristics and masses.

| Specimen temperature $T_{\text{clad}}$, °C | Effective/total oxidation duration $(\tau_{\text{eff}} / \sum \tau_{\text{eff}})$ according to correlation (2), s | Steam mass rate $G_s$, mg/s | Initial and final specimen dimension, mm | Metal mass loss $\Delta m$, mg |
|------------------------------------------|-----------------------------------------------|-------------------|----------------------------------------|-----------------------|
|                                          |                                                |                   | Outer diameter $D / D_0$ | Inner diameter $d / d_0$ | Length $L / L_0$ |
| 1 1197-1206                             | 7043 / 7043                                    | 10                | 11.47 / 11.40                      | 6.68 / 6.75           | 4.50 / 4.46       | 107.43 |
| 2 1187-1195                             | 6743 / 13786                                   | 35                | 11.46 / 11.39                      | 6.70 / 6.77           | 4.52 / 4.47       | 107.14 |
| 3 1192-1198                             | 16036 / 29822                                  | 53                | 11.47 / 11.42                      | 6.69 / 6.75           | 4.34 / 4.28       | 103.56 |
| 4 1198-1218                             | 6188 / 6188                                   | 69                | 11.46 / 11.38                      | 6.72 / 6.76           | 4.49 / 4.42       | 154.72 |
| 5 1200-1208                             | 7465 / 3653                                   | 90.9              | 11.38 / 11.34                      | 6.76 / 6.82           | 4.42 / 4.39       | 67.84  |
| 6 1200-1215                             | 8126 / 21779                                  | 98.5              | 11.34 / 11.29                      | 6.82 / 6.86           | 4.39 / 4.36       | 60.23  |
| 7 1190-1213                             | 7793 / 7793                                   | 118.1             | 11.47 / 11.35                      | 6.72 / 6.74           | 4.52 / 4.46       | 65.45  |
| 8 1205-1208                             | 12116 / 19909                                 | 33.3              | 11.35 / 11.21                      | 6.74 / 6.80           | 4.46 / 4.32       | 286.63 |
| 9 1195-1203                             | 10472 / 30381                                 | 44.6              | 11.21 / 11.17                      | 6.80 / 6.85           | 4.32 / 4.27       | 92.85  |

### Figure 1. Temperature regimes of VCPM rod cladding specimen during steam oxidation test (1200 °C, 3 h).

4 Analysis of experimental data

High temperature oxidation characteristics were compared in the form of dependency of specific VCPM volatilization rate on time. The loss of metal mass was divided by the initial full cross-section surface of rod cladding specimen because its change in time during oxidation does not exceed 2%.

The specific VCPM volatilization rate increases linearly with the rise of HT exposure time (figure 2). The measured experimental data are in good agreement with the previously ones obtained by the authors and described in [11, 12]. That fact allows temperature oxidation investigations using single specimen thus both reducing the measurement uncertainties and increasing the test reliability. The difference in the specific VCPM volatilization rate of up to 5 times at exposure time of about 2 hours (6000 – 9000 s) is explained by metals close to repeatedly used cladding specimens and their independent oxidation in the furnace high temperature zone. The fairness of that suggestion is verified by absence of cladding fragments in furnace as tests are being finished.

The test results prove that the VCPM volatilization rate out of any specimen surfaces is the same in the range of measurement uncertainties of specimen dimensions. As the obtained experimental data shows maximal effective linear rate of metal loss at the temperature of 1200 °C equal to 9.7 µm/h. Under LOCA conditions the cladding of tolerant fuel can save rod hermeticity not more than 72 hours (thermal...
mechanics processes are not considered). It is evident that using the VCPM rod claddings without protective coating is forbidden for LWR. The obtained experimental data are generalized in the form of dependence of steam-molybdenum reaction rate $K_p$ on Reynolds number of steam flow (figure 3). As it is seen the increase in steam mass rate in the investigated Reynolds numbers range $Re = 8 – 88$ at $1200°C$ does not influence the rate of SMR in the range of measurement uncertainties of experimental data. The deviation of measured values relative to the mean characteristic does not exceed ±20 %.

Figure 2. The dependency of specific cladding specimen volatilization rate on the oxidation duration at $1200°C$.

Figure 3. SMR rate constant $K_p(Re)$ at $1200°C$.

5 Theoretical analysis of oxidation mechanism

The evaluations of critical temperature of cladding specimen limiting the diffusive and kinetic regimes of Mo oxidation in water steam up to $2000 K$ were performed using molecular kinetics theory. The approach is based on the finite diffusion rate of rarefied binary gas mixture – penetration of volatile MoO$_3$ in steam.

The molybdenum trioxide molecule interaction with water steam was described by the Lennard-Jones model [13], whereas MoO$_3$ interaction potential was considered to be equal to that of Xe due to the similarity of molecular masses of substances. Thermal physics parameters of water steam were given as constant at $1273 K$. Molybdenum trioxide was described in the approach of ideal gas with temperature-dependent density. Diffusion rate of MoO$_3$ in H$_2$O was evaluated by the dependency [14]

$$D_{MoO_3} = \frac{3}{16} \cdot \left(2\pi M k T \right)^{1/2} \left[ n M \cdot \pi \sigma_{ef}^{1/2} \cdot \Omega \left(T^* \right) \right]$$

$M = M_1 \cdot M_2/(M_1 + M_2)$; $\sigma_{ef} = (\sigma_1 + \sigma_2)/2$; $T^* = T/(\epsilon k)$; $(\epsilon k)_{eff} = \left[(\epsilon k_1) \cdot (\epsilon k_2) \right]^{1/2}$; $n = p/(kT)$, where $M_1$, $M_2$ are molecular masses of diffusants ($M = 16.01$ g/mole), $\sigma_{ef}$ is effective diameter of hypothetic molecule, $m$ ($\sigma_{ef} = 3.342$ Å), $\epsilon k$ is gas mixture characteristic temperature, $K$ ($\epsilon k = 432.3 K$), $k$ is Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K); $\Omega(T^*)$ is collision integral of diffusion, rel. units, $p$ is medium pressure, atm, $T$ is temperature, K.

The diffusion flux of molybdenum trioxide mass was calculated as follows

$$K_{p_{diff}}^{MoO_3} = \rho_{MoO_3} \cdot \beta \cdot \Delta c = Sh \cdot D_{MoO_3} \cdot L \cdot \rho_{MoO_3} \cdot \Delta c,$$

where $\beta$ is mass transfer coefficient, m/s, $Sh$ is Sherwood number, rel. units, $\rho_{MoO_3}$ is molybdenum trioxide density, kg/m$^3$. According to previous investigation applied to HT oxidation of rod cladding
specimen at 1473 K the mass concentration difference \( \Delta c \) at non-oxidized surface and in the flow equals to about 3 \% [15]. Mass transfer rate was calculated by the correlation proposed for the heat transfer description at plain laminar flow (the using of heat and mass transfer analogy principle) [16]:

\[
Sh = 0.332 \cdot Re^{1/2} \cdot Pr^{1/3}
\]  
(5)

As the temperature increases the steam-molybdenum reaction rate is proved by the correlation proposed with respect to Arrhenius law [17]:

\[
K_p(T) = A \cdot \exp(-Q_A / RT)
\]

(6)

where \( A = 0.651 \times 10^3 \) is the empiric coefficient. The forced convective mass flux of molybdenum in \( \text{MoO}_3 \) form was calculated according to (4).

The total molybdenum mass flux out of specimen corresponding to the chemical SMR rate of the first order was evaluated according to (7)

\[
1/K_p = 1/K_p^{\text{kin}} + 1/K_p^{\text{diff}}
\]

(7)

The calculation results of diffusion, kinetic additives of SMR rate as well as the total interaction rate of molybdenum with water steam in the temperature range of 1000 – 2000 K are shown in figure 4. The intersection point of \( K_p^{\text{kin}} \) and \( K_p^{\text{diff}} \) dependencies characterizes the critical temperature of oxidation regime change of cladding specimen. The computation results of diffusion, kinetic additives of SMR show that under minimal realized steam flow rate of 10 mg/s corresponding to Reynolds number \( Re \sim 6.9 \) the change of oxidation regime is reached at critical temperature of 1523 K. Thus, the theoretical analysis confirms that the influence of steam flow rate on the cladding specimen oxidation rate under test conditions at 1473 K will appear at reduced Reynolds number \( Re < 5 \) that is respect to \( G_s < 7 \text{ mg/s} \).

Summarizing the theoretical analysis it might be argued that in the experimentally investigated steam mass rate range the intensity of SMR is limited by kinetic regime. The diffusion regime is expected to limit SMR under the temperatures exceeding 1400 °C. This theoretical conclusion requires further verification.

![Figure 4](imageurl)

**Figure 4.** The influence of diffusion and kinetic additives on the SMR rate constant in the temperature range of up to 2000 K.

**Conclusion**

1. The series of HT steam oxidation tests at GASPAR facility of cladding specimens made of VCPM in the temperature range of 900 – 1200°C, exposure durations of up to \( 24.6 \times 10^3 \text{ s} \) and oxidant mass rates of up to 120 mg/s was carried out.
2. It has been experimentally established that intensity of steam-molybdenum reaction at 1200°C determined by the reaction rate is a constant value \( K_{pMo} = 2.31 \times 10^{-5} \text{ kg/(m}^2\text{·s)} \) within the range of experimental data variation of \( \pm 20 \% \).
3. It has been shown that metal volatilization rate at 1200°C does not depend on steam mass rate in the range of (10-120) mg/s that respects to gas mixture laminar flow close to cladding specimen at \( Re = 8 - 88 \).
4. It has been theoretically evaluated and experimentally verified that the diffusion regime during molybdenum oxidation by steam laminar flow at 1200°C in the practically significant Reynolds
numbers range is not realized. As the temperature rises up to 1400°C the boundary of diffusion regime is moved to critical Reynolds number $Re_{cr} = 25-30$.

5. The refinement of steam-molybdenum reaction rate taking into consideration the kinetic and diffusion regimes requires more valid data on the molecular kinetic and thermophysical properties of MoO$_3$.

6. Despite the use of non-covered rod claddings made of molybdenum to LWR the obtained results is in practical importance for the conservative evaluation of tolerant fuel performance under LOCA whereas the protective coating has lost its protective properties.

**Acknowledgments**

Authors would like to thank Popov E.B. for the valuable discussions of obtained results and Deryabin I.A. for the finite element analysis of oxidation process.

**References**

[1] Cheng B, Chou P, Kim Y 2016 Development of mo-based accident tolerant LWR fuel cladding IAEA-TECDOC-1797-Conf 2014 p 66-78

[2] Lee Y 2013 Safety of Light Water Reactor Fuel with Silicon Carbide Cladding PhD thesis Massachusetts Institute of Technology

[3] Cheng Bo 2015 Refractory metal cladding and Mo-alloy development for accident tolerant fuel. OECD/NEA Expert Group on ATF for LWRs – Task force 2 March 3 - 5

[4] Ott L, Robb K, Wang D 2014 Preliminary assessment of accident-tolerant fuels on LWR performance during normal operation and under DB and BDB accident conditions. Journ of Nuc. Mats. 448 520–533

[5] Chirkin V S 1968 Thermal physical properties of materials in nuclear engineering Atomizdat Reference book

[6] Mechanical Engineering Encyclopedia in 40 volumes. Volume IV-25. 2005 Mechanical Engineering Nuclear Engineering Book 1 "Mechanical Engineering"

[7] Kuznetsov Yu V 1989 Heat transfer in the problem of safety of nuclear reactors. Energoatomizdat 286 p

[8] Godin A, Tenishev A, Novikov B 2008 Physical Materials Science Volume 6 Part 2 Nuclear Fuel Materials, MEPHl 604 p

[9] Kilpatrick M, Lott S 1965 Reaction of flowing steam with refractory metals I Molybdenum (1100 – 17000) Journal of Physical Chemistry V 69 n 5 , p. 1638 – 1640

[10] Nelson A, Sooby E 2014 High temperature oxidation of molybdenum in water vapor environments J Nuclear Materials No 448 pp 441–447

[11] Bazyuk S, Kiselev D, Kuzma-Kichta Yu, Mokrushin A et al. 2017 Investigation of the thermophysical and corrosion characteristics of the shells of operating and promising fuel elements of light-water reactors in an accident with loss of coolant Engineering Physics Journal Volume 90 No. 1, 247-255 Institute of Heat and mass transfer them. A.V. Lykova NAS of Belarus (Minsk) ISSN: 0021-0285

[12] Bazyuk S, Parshin N, Popov E et al. 2017 Investigation of the corrosion characteristics of standard and prospective claddings of fuel elements of light-water reactors under the conditions of LOCA 10th ISTC "Safety of NPPs with VVER" OKB Gidopress.

[13] Lennard-Jones J 1924 Proc. Roy. Soc v. A 106 p. 463

[14] Hirschfelder J, Curtiss Ch, Bird R Molecular theory of gases and liquids John Wiley and sons, INC., New York Chapmann And Hall, Lim., London 1954

[15] Bazyuk S, Parshin N, Popov E, Soldatkin D et al. 2017 Oxidation investigation of cladding specimens for regular and accident tolerant fuel rods under LOCA conditions IOP Conf. Series: Journal of Physics: Conf. Series 891 012180. doi :10.1088/1742-6596/891/1/012180

[16] Petukhov B, Genin L, Kovalev S, Soloviev S 2003 Heat transfer in nuclear power plants MPEI Publishing House 500 p

[17] Stiller W 1989 Arrhenius Equation and Non-Equilibrium Kinetics B. G. Teubner
Verlagsgesellschaft, Leipzig

[18] Reid R Prausnitz Sherwood Th 1977 The properties of gases and liquids McGraw-Hill Book Co. Third edition

[19] Frank-Kamenetsky D 1987 Diffusion and heat transfer in chemical kinetics Nauka 502 p.