PRE-OXIDATION EFFECT OF A ZIRCONIUM-SILICIDE SPUTTERED SURFACE ON BOILING PERFORMANCE AND OXIDATION RESISTANCE

G.C. LEE, H. NOH, M.R. KIM
Department of Mechanical Engineering, POSTECH
77 Cheongam-Ro, 37673 Pohang – Republic of Korea

T.K. Kim, H.S. PARK, M.H. KIM
Division of Advanced Nuclear Engineering, POSTECH
77 Cheongam-Ro, 37673 Pohang – Republic of Korea

H. YEOM, H. JO, K. SRIDHARAN
Department of Engineering Physics, University of Wisconsin-Madison
1500 Engineering Drive, WI 53706 Madison – USA

ABSTRACT

Thin zirconium silicide ($ZrSi_2$) material was coated on present cladding substrate, Zircaloy-4. At 700 °C air environment, the $ZrSi_2$ coating prevented thermal oxidation and thereby protected the underlying Zircaloy-4 substrate. To investigate the boiling characteristics, the pool boiling experiment with saturated water and Leidenfrost experiment with low weber number were examined under atmospheric pressure condition. The experimental results showed that by thermal oxidation, critical heat flux and Leidenfrost temperature were not changed on $ZrSi_2$ coated surface whereas the results were changed on uncoated Zircaloy-4 substrate. The surface parameters were changed while oxidation process and led to the transition of boiling parameters.

1. Introduction

Zirconium alloy fuel cladding is widely used in light water reactors (LWRs) because of its low thermal neutron absorption cross section, good mechanical properties, and corrosion resistance in normal operating conditions [1]. The prime interest in nuclear safety is to prevent radiation leakage and core melt-down accidents. Loss-of-coolant accidents (LOCAs) cause increase in the temperature of the reaction core, so fuel cladding is exposed to high-temperature water and steam. In such conditions, the zirconium cladding reacts with water; the reaction produces hydrogen that dissolves in the cladding and causes embrittlement [2]. To improve the reliability of nuclear safety systems, an accident-tolerant fuel cladding (ATFC) may mitigate thermal oxidation at high temperature, and cladding embrittlement under LOCA [3]. Zirconium silicide is a potentially attractive candidate for ATF due to its high melting temperature, low neutron penalty, and good oxidation resistance [4]. In order to apply the ATF material in practice, assessment of thermal-hydraulics performance should be considered. Under nucleate boiling regime, the cladding surface can achieve efficient heat removal. However, after critical heat flux (CHF), the vapor layer covers the cladding surface and this results in rapid degradation of heat flux and increase of cladding temperature During a LOCA, this post-CHF regime can happen until an emergency core cooling system (ECCS) actively cools the system. The reactor core is reflooded with coolant water and degradation of heat flux

recovers after minimum film boiling temperature (T_{MFB}) or Leidenfrost temperature (T_{LFP}). In recent boiling studies, the surface modification technique and their effects on the boiling performance have been actively carried out [5-7]. By the oxidation process, the surface parameter and boiling characteristics could be changed. Due to changed morphologies of the surface, the CHF, T_{MFB}, and T_{LFP} were increased on modified surfaces [8-10]. Therefore, the surface parameter change due to oxidation and the resulting boiling performance needs to be analyzed [11].

The major goal of this study is preliminary assessment of zirconium silicide coatings respect to the boiling performance and oxidation resistance. The oxidation is conducted at 700 °C air environment on zirconium silicide coated Zircaloy-4 and uncoated Zircaloy-4 surface. The pool boiling experiment with saturated water and Leidenfrost experiment with low weber number were examined under atmospheric pressure condition to measure the boiling parameters.

2. Materials and Methods

The zirconium silicide (American Elements Inc.) coatings were deposited on Zircaloy-4 using magnetron sputter deposition technique [12]. To ensure constant coating procedures, the Zircaloy-4 substrates were prepared by mechanical polishing and chemically cleaning for removing surface contaminants. The deposition process was performed with constant rotating stage (10 rpm) in the room temperature (19 °C) [4, 12]. To investigate the effect of oxidation to the boiling performance, pre-oxidation was conducted on the zirconium silicide ($ZrSi_2$) coated Zry-4 and uncoated Zry-4 surface. The oxidation environment with heating rate 5 °C/min, duration 1 hour at 700 °C, and cooling rate ~ 1.6 °C/min was used.
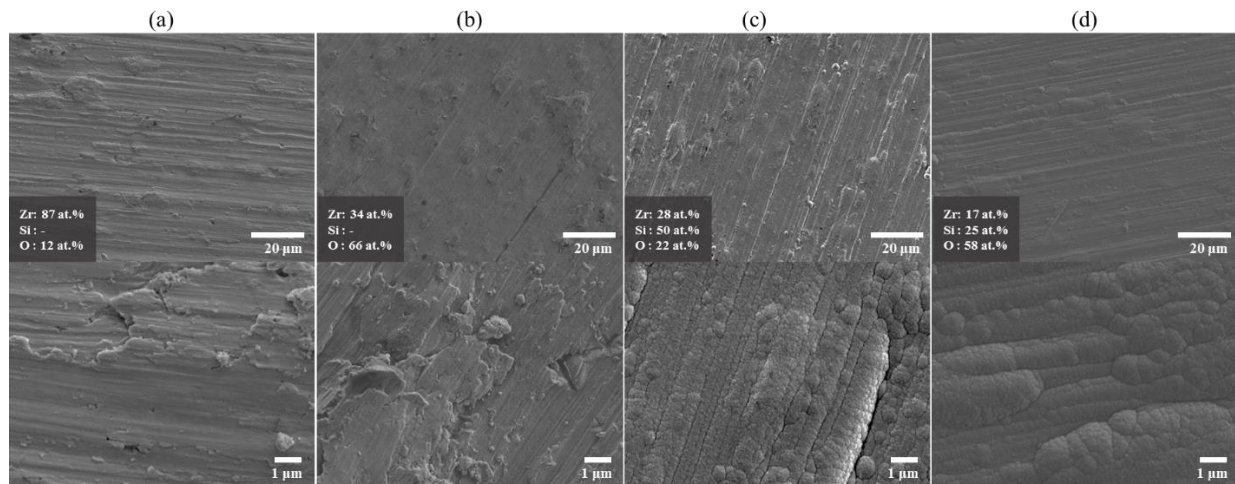

Figure 1. Field-emission scanning electron microscope images with energy dispersive x-ray spectroscopy (a) Zircaloy-4 (Zry-4), (b) Pre-oxidized Zry-4 (OS Zry-4), (c) $ZrSi_2$ coated Zry-4 (ZrSi-Zry), (d) Pre-oxidized ZrSi-Zry (OS ZrSi-Zry).

Four test specimen, Zircaloy-4 (Zry-4), Pre-oxidized Zry-4 (OS Zry-4), ZrSi coated Zry-4 (ZrSi-Zry), and Pre-oxidized ZrSi-Zry (OS ZrSi-Zry) were used. The surface morphologies were investigated by a field-emission scanning electron microscope. The oxygen components increased about 54 % on Zry-4 and 36 % on ZrSi-Zry after pre-oxidation. The surface roughness was measured using a surface profiler (Alpha-Step IQ; KLA Tencor) at three times for each surface (table 1). The roughness was slightly increased after pre-oxidation.
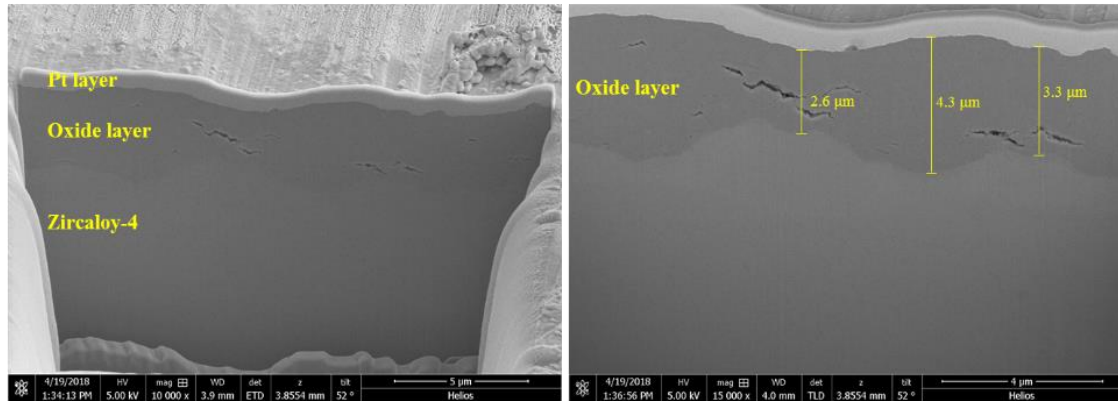
Table 1. Surface roughness for test specimen.

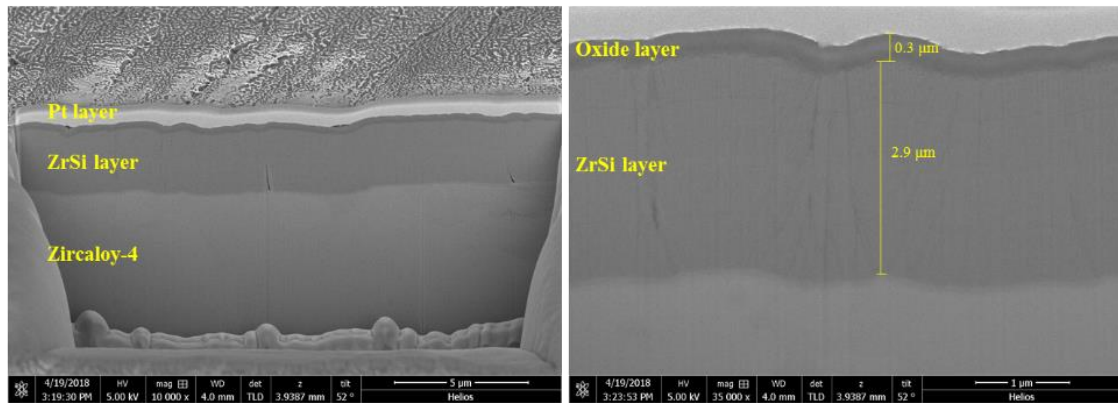| Test specimen	R_a (nm)		R_q (nm)		R_{max} (nm)	
	Average	Stand deviation	Average	Stand deviation	Average	Stand deviation
Zry-4	153.7	13.8	202.3	10.5	1119.0	124.4
OS Zry-4	207.0	31.2	270.0	46.0	1492.7	246.7
ZrSi-Zry	187.7	11.5	241.7	15.3	1372.3	88.6
OS ZrSi-Zry	204.3	56.0	252.0	58.0	1230.7	256.7

3. Results
3.1 Oxidation resistance

Figure 2. Cross section view by Focused Ion Beam (FIB) of pre-oxidized test specimen (OS Zry-4 and OS ZrSi-Zry); Protective Pt layer is deposited before ion beam processing.

Focused ion beam (FIB; Helios, FEI) was used for oxide layer measurement. To preventing surface damage, protective platinum layer was deposited before ion beam processing. The images on fig. 2 shows the excavated pit by ion beam, having about 20 μm width, and enlarged cross section view. The pore structure within the oxide layer was detected on OS Zry-4. On OS ZrSi-Zry, about 0.3 μm oxide layer was formulated on outmost surface, but no pore or crack structure was found. A small portion of $ZrSi_2$ coating layer (0.1 μm) was eliminated during oxidation. However, most of ZrSi coating layer was preserved after pre-oxidation, thereby protecting underlying Zircaloy-4 substrate from oxidation. EDS mapping results supported
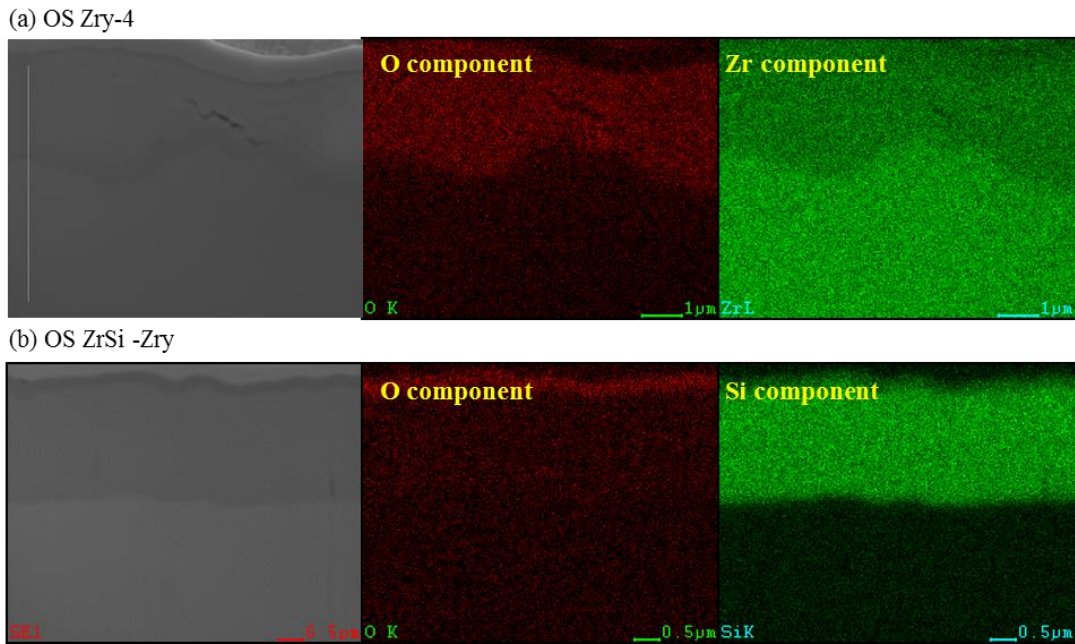
above results (Fig. 3).

(a) OS Zry-4

(b) OS ZrSi -Zry

Figure 3. EDS mapping results of pre-oxidized test specimen (OS Zry-4 and OS ZrSi-Zry) after pre-oxidation.

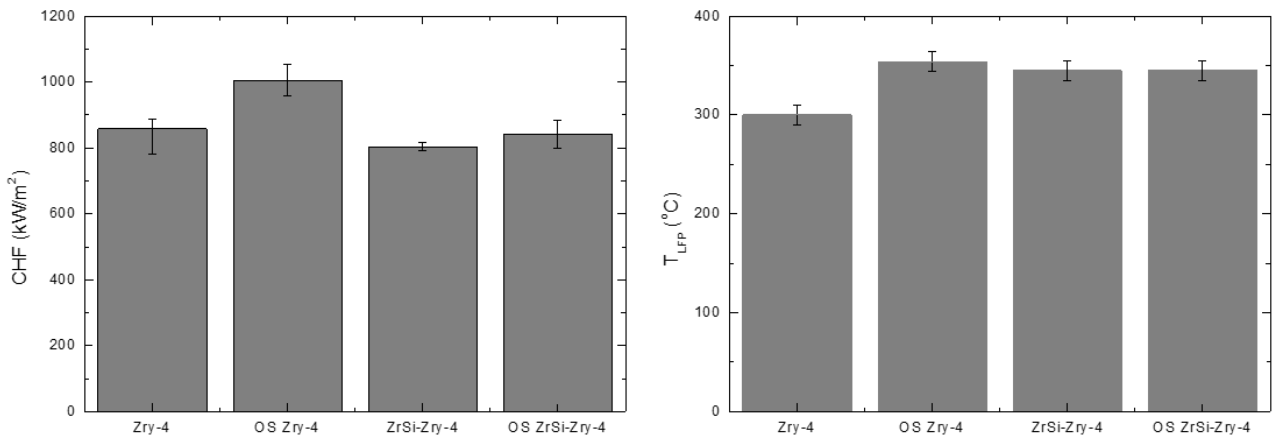## 3.2 Boiling characteristics: CHF and T_{LFP}

Figure 4. Pool boiling CHF results (Left) and Leidenfrost temperature (Right) for test specimen

CHF for test specimens were evaluated (fig. 4, left). Comparing Zry-4 and ZrSi-Zry, there was no significant change in CHF, which represents $ZrSi_2$ coating had less effect on CHF change. Receding contact angles (θ_r) of Zry-4 and ZrSi-Zry were similar as 17.5 ° and 12.0 °. CHF is known as having dependency on $cos\theta_r$ for flat surfaces [13], and accordingly the small CHF difference between Zry-4 and ZrSi-Zry could be explained.

4

However, after oxidation, a meaningful change on CHF of Zry-4 specimens was observed unlike ZrSi-Zry specimens. Surface roughness is known as one of the most effective surface parameters on CHF determination. Usually, increased CHF was reported on modified surfaces with high surface roughness [6,14,15]. There are several discussion on the CHF increase mechanism of surface roughness. Chu et al. suggested CHF modeling with force balance introducing the concept of the effective contact line length of a bubble [6]. According to this model, surface roughness gives long contact line length around a bubble, and it results in large force required for horizontal expansion of a bubble. They postulated CHF occurs when bubble expends to a horizontal direction by vigorous evaporation. Therefore, high surface roughness can delay CHF occurrence in boiling situation. Son et al. reported higher CHF with increasing surface roughness on Cr-sputtered surfaces [15]. They adopted DC magnetron sputtering method to deposit thin layer of Cr with nano-spikes on the boiling surface. Surface roughness was controlled by changing condition of surface finishing by emery papers with grit numbers from 320 to 4,000. As a result, they could fabricated Cr coated surfaces with 38 ~ 258 nm of arithmetic averaged roughness, R_a. R_a and CHF had a relation as monotonic increase in their experimental range. R_a values in this research are within 150 ~ 210 nm, which falls within the experimental range of Son et al. Therefore, we could assume that for each Zry-4 and ZrSi-Zry, CHF change by oxidation resulted from increased surface roughness.

The T_{LFP} result on Zry-4 was consistent with previous experimental data under similar condition [16]. They used the same material, Zry-4 with low weber number condition under 10. Comparing Zry-4 and ZrSi-Zry, T_{LFP} was increased about 45 °C on ZrSi-Zry. In the pool quenching experiment in atmospheric saturated water condition, the consistent results (increased T_{MFB} about 20 °C) was reported [12]. The rewetting temperature (T_{MFB} or T_{LFP}) depends on the thermal properties of surface [17-18]. The increased T_{MFB} was explained by lower thermal conductivity during sputtering process [12].

The surface roughness is the one of the major factor for influencing the rewetting temperature. In film boiling regime, the intermittent liquid-solid contact is promoted by surface roughness poking through the thin vapor layer [19-21]. As the surface roughness increases, a thicker vapor layer, and hence a higher surface temperature, is required to keep the film boiling state [22]. Therefore, increased surface roughness by thermal oxidation might influence the T_{LFP} results. However, the vapor layer thickness was reported as order of tens of micro meters [23-24] and R_a values in this research (within 150 ~ 210 nm) is small compared with reported vapor layer thickness for inducing intermittent liquid-solid contact. Then what mainly causes the T_{LFP} increase on oxidized surface? Consider a surface whose temperature is heated up with high temperature. When a droplet approaches and touches the surface, a vapor layer will begin to form under the droplet [24]. Upon impact of the drop, this surface temperature begins to decrease by cool liquid water. At that moment, the liquid-solid interface temperature is determined by thermal effusivity defined as $(k\rho c_p)^{1/2}$ and temperature of liquid and solid [25]. If the thermal effusivity of solid surface decrease, the liquid solid interface temperature decreases [26]. Therefore the formation of oxide layer with lower thermal effusivity, make the effective interface temperature lower and thus requires higher surface temperature for film boiling state.

4. Conclusion

Evaluation of the zirconium silicide material as the candidate for accident tolerant fuel cladding was investigated through oxidation resistance, pool boiling CHF and T_{LFP}. For practical application, thin zirconium silicide coating with 3 μm thickness was deposited on present cladding material, zirclaoy-4 substrate. The summary of our findings obtained in the present study are as follows:

- Oxidation results showed the good oxidation resistance for thin zirconium silicide material coating. On uncoated zircloay-4 specimen, oxide layer with 2~5 μm thickness and internal

pore structure were found. In the contrast, zirconium silicide coating protect the underlying zircloay-4 substrate from thermal oxidation without crack or damage.

- The coating itself did not influence the CHF results. However, CHF results were changed by the pre-oxidation. After pre-oxidation, CHF of uncoated Zircaloy-4 surface increased about 17 % but CHF of the ZrSi coating surface was not changed after pre-oxidation. The CHF increase was explained by surface roughness of oxide layer.
- The T_{LFP} was increased after ZrSi coating by reduced thermal conductivity. Likewise the trend of CHF results, the T_{LFP} on uncoated Zircaloy-4 surface increased after pre-oxidation. The T_{LFP} increase was explained by the thermal properties with liquid-solid interface temperature.
- From the experimental results on CHF and T_{LFP} in this study, we could confirm that the surface parameters, their effective ranges, and major mechanisms affecting the boiling performance are different for each boiling regime.

5. References

[1] Sabol, G. P., Comstock, R. J., Weiner, R. A., Larouere, P., & Stanutz, R. N. (1994, January). In-reactor corrosion performance of ZIRLO™ and zircaloy-4. In Zirconium in the nuclear industry: Tenth International Symposium. ASTM International.

[2] Rebak, R. B. (2015). Alloy selection for accident tolerant fuel cladding in commercial light water reactors. Metallurgical and Materials Transactions E, 2(4), 197-207.

[3] Kurata, M. (2016). Research and development methodology for practical use of accident tolerant fuel in light water reactors. Nuclear Engineering and Technology, 48(1), 26-32.

[4] Yeom, H., Maier, B., Mariani, R., Bai, D., Fronek, S., Xu, P., & Sridharan, K. (2017). Magnetron sputter deposition of zirconium-silicide coating for mitigating high temperature oxidation of zirconium-alloy. Surface and Coatings Technology, 316, 30-38.

[5] Kim, H., & Kim, M. (2009). Experimental study of the characteristics and mechanism of pool boiling CHF enhancement using nanofluids. Heat and Mass Transfer, 45(7), 991-998.

[6] Chu, K. H., Enright, R., & Wang, E. N. (2012). Structured surfaces for enhanced pool boiling heat transfer. Applied Physics Letters, 100(24), 241603.

[7] Kim, S. H., Lee, G. C., Kang, J. Y., Moriyama, K., Kim, M. H., & Park, H. S. (2015). Boiling heat transfer and critical heat flux evaluation of the pool boiling on micro structured surface. International Journal of Heat and Mass Transfer, 91, 1140-1147.

[8] Ahn, H. S., Lee, C., Kim, H., Jo, H., Kang, S., Kim, J., ... & Kim, M. H. (2010). Pool boiling CHF enhancement by micro/nanoscale modification of zircaloy-4 surface. Nuclear Engineering and Design, 240(10), 3350-3360.

[9] Kang, J. Y., Kim, S. H., Jo, H., Park, G., Ahn, H. S., Moriyama, K., ... & Park, H. S. (2016). Film boiling heat transfer on a completely wettable surface with atmospheric saturated distilled water quenching. International Journal of Heat and Mass Transfer, 93, 67-74.

[10] Lee, G. C., Kang, J. Y., Park, H. S., Moriyama, K., Kim, S. H., & Kim, M. H. (2017). Induced liquid-solid contact via micro/nano multiscale texture on a surface and its effect on the Leidenfrost temperature. Experimental Thermal and Fluid Science, 84, 156-164.

[11] Buongiorno, J. (2014). Can corrosion and CRUD actually improve safety margins in LWRs?. Annals of Nuclear Energy, 63, 9-21.

[12] Yeom, H., Lockhart, C., Mariani, R., Xu, P., Corradini, M., & Sridharan, K. (2018). Evaluation of steam corrosion and water quenching behavior of zirconium-silicide coated LWR fuel claddings. Journal of Nuclear Materials, 499, 256-267.

[13] Kandlikar, S. G. (2001). A theoretical model to predict pool boiling CHF incorporating effects of contact angle and orientation. Journal of Heat Transfer, 123(6), 1071-1079.

[14] Seo, G. H., Jeun, G., & Kim, S. J. (2016). Enhanced pool boiling critical heat flux with a FeCrAl layer fabricated by DC sputtering. International Journal of Heat and Mass Transfer, 102, 1293-1307.

[15] Son, H. H., Seo, G. H., Jeong, U., & Kim, S. J. (2017). Capillary wicking effect of a Cr-sputtered superhydrophilic surface on enhancement of pool boiling critical heat flux. International Journal of Heat and Mass Transfer, 113, 115-128.

[16] Kim, S. H., Ahn, H. S., Kim, J., Kim, M. H., & Park, H. S. (2014). Experimental study of water droplets on over-heated nano/microstructured zirconium surfaces. Nuclear Engineering and Design, 278, 367-376.

[17] Kikuchi, Y., Hori, T., & Michiyoshi, I. (1985). Minimum film boiling temperature for cooldown of insulated metals in saturated liquid. International journal of heat and mass transfer, 28(6), 1105-1114.

[18] Kang, J. Y., Kim, T. K., Lee, G. C., Kim, M. H., & Park, H. S. (2018). Quenching of candidate materials for accident tolerant fuel-cladding in LWRs. Annals of Nuclear Energy, 112, 794-807.

[19] Kim, H., Truong, B., Buongiorno, J., & Hu, L. W. (2011). On the effect of surface roughness height, wettability, and nanoporosity on Leidenfrost phenomena. Applied Physics Letters, 98(8), 083121.

[20] Kwon, H. M., Bird, J. C., & Varanasi, K. K. (2013). Increasing Leidenfrost point using micro-nano hierarchical surface structures. Applied Physics Letters, 103(20), 201601.

[21] Yeom, H., Jo, H., Johnson, G., Sridharan, K., & Corradini, M. (2018). Transient pool boiling heat transfer of oxidized and roughened Zircaloy-4 surfaces during water quenching. International Journal of Heat and Mass Transfer, 120, 435-446.

[22] Bernardin, J. D., & Mudawar, I. (1999). The Leidenfrost point: experimental study and assessment of existing models. Journal of Heat Transfer, 121(4), 894-903.

[23] Biance, A. L., Clanet, C., & Quéré, D. (2003). Leidenfrost drops. Physics of Fluids, 15(6), 1632-1637.

[24] Lee, G. C., Noh, H., Kwak, H. J., Kim, T. K., Park, H. S., Fezzaa, K., & Kim, M. H. (2018). Measurement of the vapor layer under a dynamic Leidenfrost drop. International Journal of Heat and Mass Transfer, 124, 1163-1171.

[25] Eckert, E. R., & Drake, R. M. (1972). Analysis of Heat Transfer. McGraw-Hill.

[26] Baumeister, K. J., & Simon, F. F. (1973). Leidenfrost temperature—its correlation for liquid metals, cryogens, hydrocarbons, and water. Journal of Heat Transfer, 95(2), 166-173.

Acknowledgement