

Temperature-dependent Thermal Conductivity Model for Simulated Crud with Varying Its Porosity using Experimental Data Fitting

Hee-Sang Shim *, Do Haeng Hur, Soon-Hyeok Jeon, Sang-Yeob Lim

Materials Safety Technology Research Division, KAERI, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Korea

*Corresponding Author: hshim@kaeri.re.kr

***Keywords :** Fuel Clad, Crud, Thermal Conductivity, Temperature, Porosity

1. Introduction

Crud, which is the corrosion products deposited on fuel cladding surfaces, is mainly formed when the sub-cooled nucleate boiling (SNB) occurs on a heated fuel cladding surface [1]. Crud was initially named Chalk River Unidentified Deposit, a term referring to the oxide film formed on the surface of nuclear fuel cladding, which was obtained in Canadian nuclear power plant. However, it is now also called as Corrosion Related Unidentified Deposit. The chemical composition of crud is mainly nickel ferrite ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$) in non-stoichiometric form or magnetite (Fe_3O_4), but types of nickel oxide, zirconium oxide or boron-composites is also found on the surface of high duty or long-term operated fuels [2]. The deposit sources came from reactor coolant system (RCS) surface. The RCS materials were corroded, released and transported with the coolant into the core. The corrosion products were deposited and activated in fuel cladding surface. In addition, a part of activated crud was released, transported, deposited to the ex-core surface. Therefore, crud causes the problems of fuel integrity such as crud-induced power shift (CIPS) or crud-induced localized corrosion (CILC), as well as the activity buildup of RCS. CIPS occurs due to boron accumulation into porous crud structure and decrease the core shutdown margin [3,4]. In addition, CILC is a problem in which corrosion of fuel cladding is locally accelerated because the crud having low thermal conductivity obstructs heat transfer from clad surface to coolant. Recently, a lot of nuclear power plants have been employing strategies for the power uprate, high burn-up, and long-term operation of nuclear power plant for economical electricity generation [5,6]. These operation strategies result increase in the thickness of fuel cladding oxide and the deposit amount of fuel crud. In addition, the threat to nuclear fuel integrity is increasing due to the increase in crud.

Recently, nuclear regulatory agencies such as KINS or NRC are strengthening the fuel safety criteria for design basis accidents such as loss of coolant accident (LOCA) or reactivity initiated accident (RIA) because the thickness increase of fuel cladding oxide and crud can affect more seriously to the fuel integrity in accident conditions than normal operation condition [7]. In addition, they have demand to reflect the actual thermal resistances of fuel cladding oxide and crud, which have

previously used with a constant value or a calculated value, into the computation code for evaluating fuel integrity. However, a measurement and a calculation of thermal resistance of crud layer are not simple because the crud consists of complex chemical composition and various geometry due to its deposition environment as well as deposited on curved surface. Thereby, few studies have been conducted on the measurement of crud's thermal properties [8-10].

In this study, in order to reduce the analysis error of thermal properties, crud layer of nickel ferrite was deposited on flat plate having same properties with commercial fuel cladding under simulated primary condition. The density, specific heat capacity and thermal diffusivity of crud layer were measured using pycnometer, differential scanning calorimetry (DSC), and laser flash analyzer (LFA) as a function of temperature. In addition, we derived a temperature-dependent thermal conductivity model based on these experimental data fitting.

2. Experimental Methods

Porous crud layers were deposited on Zr1.0Nb-1.0Sn-0.1Fe metallic plates using a simulated primary loop with controlling cartridge heater temperature. Heater to control the heat flux of metallic plate with a dimension of 10 mm x 10 mm x 0.48 mm was specially designed as shown in Fig. 1. Prior to crud deposition, the specimen is cleaned with ultrasonication in acetone, alcohol and deionized water for each 10 min. The plate specimen was mounted on heater surface and it was inserted into the test section. The primary water was prepared by dissolving LiOH of 2 ppm and H_3BO_3 of 1,000 ppm into deionized water. The dissolved oxygen and hydrogen concentration in coolant were controlled to less than 5 ppb and remained at 35 cc/kg- H_2O , respectively. The primary water was circulated with flow rate of 100 cc/min. The crud source was prepared by dissolving 600 ppm of ethylenediaminetetraacetic acid (EDTA) disodium Nickel(II) salt hydrate and 800 ppm of iron(II) acetate tetrahydrate into deionized water. The crud source solution was supplied to the test section at an injection rate of 1.0 cc/min when the coolant temperature and pressure in test section was stabilized at 328°C and at 130 bar, respectively. The surface temperature of metallic substrate surface was maintained at 345, 350, and 355°C, respectively, in order to control the SNB

condition. Then, the heat flux was calculated with 5.3, 6.1, 6.8 W/cm² for 345, 350 and 355°C, respectively, from Gunther's equation [11]. The crud deposition was performed for 25 days.

To investigate the porosity effect on thermal conductivity of crud layer, dense crud film having chemical composition and thickness similar with that of porous crud were prepared using RF-magnetron sputtering system. Sputtering was performed using both NiO and Fe₃O₄ targets under argon gas atmosphere at 300°C for 112 h. The RF power of NiO and Fe₃O₄ targets was controlled to 100W and 400 W, respectively. The dense crud was deposited to be a thickness of 50 μm.

The surface morphology and chemical composition of cruds deposited on fuel cladding material were observed using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy(EDS). The cross-sectional images of cruds were measured using focused ion beam (FIB)-SEM. Crystallinity of cruds were analyzed using X-ray diffraction (XRD). Thermal diffusivity, specific heat capacity and density were measured using LFA, DSC and He gas pycnometer, respectively. The thermal conductivity (λ) of cruds were obtained by multiplying the thermal diffusivity (α), specific heat capacity (c_p), and density (ρ). The experimental data-based fitting model was derived using Origin software, adjusting the parameters.

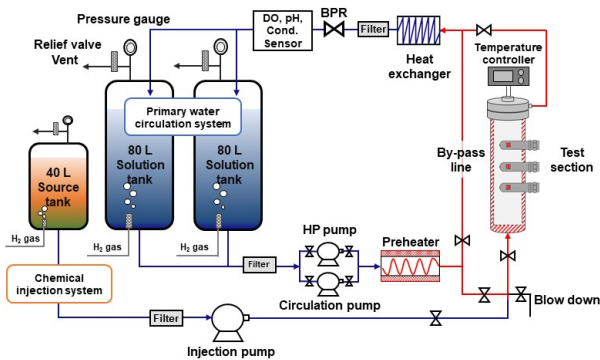


Fig. 1. A Schematic of the simulated crud deposition loop for evaluating its thermal properties

3. Results & Discussion

Fig. 2 shows the SEM surface images of dense and porous cruds. The surface of crud coated using co-sputtering system is very clean and smooth as shown in Fig. 2(a), although it is observed at high magnification compare to other samples. However, cruds deposited in simulated PWR primary loop show a rough surface, which consists of many protruding structures and holes as shown in Figs. 2(b)-2(d). This is probably because crud layers are deposited under boiling condition. The protrusion density of crud surface slightly increases as the surface temperature of substrate increases. The chemical composition of four crud sample, which was analyzed using SEM-EDS, was summarized in Table 1.

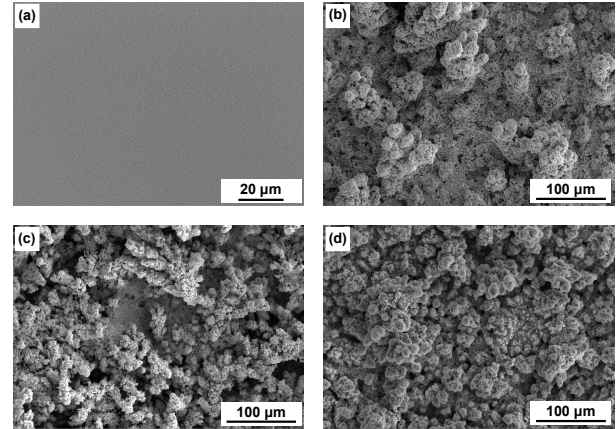


Fig. 2. SEM surface micrographs of (a) dense crud and porous cruds deposited at the specimen surface temperature of (b) 345°C, (c) 350°C and (d) 355°C.

Table 1. Chemical composition of deposited cruds

Sample	Chemical comp. (at%)			Stoichiometry
	Ni	Fe	O	
Sputtered	10.33	32.83	56.84	Ni _{0.72} Fe _{2.30} O _{3.98}
345°C	10.63	33.06	56.31	Ni _{0.74} Fe _{2.31} O _{3.94}
350°C	10.18	32.91	56.92	Ni _{0.71} Fe _{2.30} O _{3.98}
355°C	10.52	32.50	56.98	Ni _{0.74} Fe _{2.27} O _{3.99}

The chemical composition was obtained from average value of each crud samples measured at least in three locations. The stoichiometry of all crud samples is almost similar with Ni_{1-x}Fe_{2+x}O₄ and the x is in the range of 0.26 to 0.30, which is easily measured in cruds obtained from nuclear fuel.

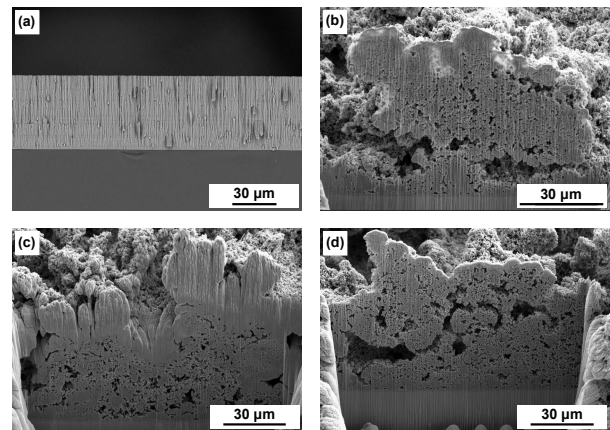


Fig. 3. SEM cross-sectional micrographs of (a) dense crud and porous cruds deposited at the specimen surface temperature of (b) 345°C, (c) 350°C and (d) 355°C.

Fig. 3 displays the cross-sectional SEM images of cruds deposited using sputtering and crud deposition loop. To analyze average porosity and thickness of crud layers, the specimens were prepared by splitting the crud sputtered on silicon wafer and by machining cruds deposited in PWR primary loop with FIB, respectively.

The pore is not observed in sputter-deposited crud layer and it is dense film with uniform thickness of about 50 μ m as shown in Fig. 4(a). However, cruds deposited in PWR primary loop shows different thickness for the location and pores having various size as shown in Figs. 4(b)-4(d). The average porosity and thickness of four crud layers are compared together in Fig.4. Average porosity is measured by 0 for dense film and by 22.5% for 345 $^{\circ}$ C crud, 27.3% for 350 $^{\circ}$ C crud, 31.0% for 355 $^{\circ}$ C crud, respectively. This means that the porosity of crud increases with increasing cartridge heater temperature due to the acceleration of boiling, which is one of the root causes for crud deposition.

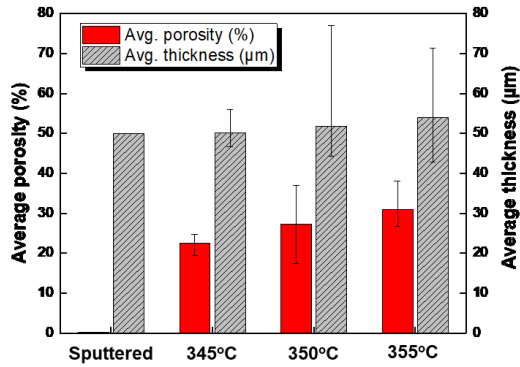
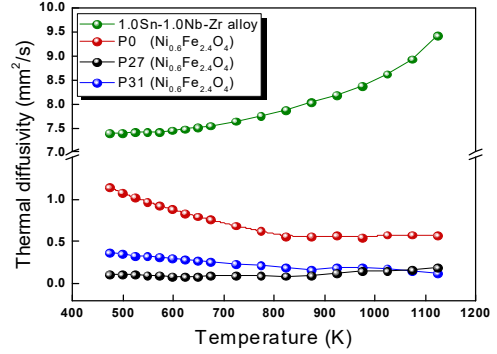


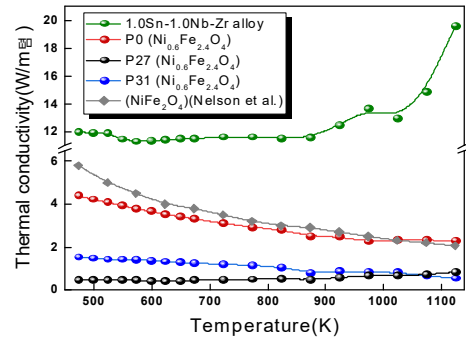
Fig. 4. Average porosity and thickness of crud layers measured from FIB-SEM images.

Fig. 5 shows the thermal diffusivity and thermal conductivity of zirconium alloy cruds with different porosity as a function of temperature. Thermal diffusivity of zirconium alloy metal exponentially increases but that of crud decreases with increasing the temperature as shown in Fig. 5(a). Thermal diffusivity of zirconium alloy metal is larger by 7 times with 7.394 mm²/s at 473 K than that of dense crud with 1.143 mm²/s. The diffusivity of crud decreases about 70% with increase in porosity from 1.143 mm²/s to 0.37 mm²/s at 473 K. This means that the thermal resistance of crud layer increases due to increased porosity. To derive the temperature-dependent thermal conductivity model, the experimental data fitting was performed by using Origin software and the fitting results were summarized with models in some references in Table 2.

Although the thermal conductivity temperature model of nickel ferrite is extremely limited, its thermal conductivity has an inverse relationship with temperature, as described at the equations for porosity of 5% and 40% in Table 2 [9,12]. On the other hand, the thermal conductivity of nickel ferrite crud obtained in this study can be derived in the form of a quadratic equation of temperature. That is, the thermal conductivity of nickel ferrite decreases in proportion to the square of the temperature as the temperature increases. In addition, the decreasing rate of thermal conductivity with temperature is greater than that proposed by Nelson's temperature model [12], and the thermal conductivity measured at the reactor core average temperature of 327 $^{\circ}$ C is also somewhat lower.



(a)



(b)

Fig. 5. (a) Thermal diffusivity and (b) thermal conductivity of zirconium alloy and cruds with different porosity in the temperature range from 473K to 1123K.

Table 2. The temperature-dependent thermal conductivity model of nickel ferrite having different porosity

Porosity (%)	Thermal cond. (W/m·K)	Thermal conductivity model $\lambda_{crud} = F(T)$ (473~1123K)	Ref.
0	4.39-2.30	$\lambda_{crud} = 8.5663 - 1.1 \cdot 10^{-2}T + 5.0 \cdot 10^{-6}T^2$	This work
5	5.8-2.0	$\lambda_{crud} = (4.371 \cdot 10^{-4} + 2.751 \cdot 10^{-2}T)^{-1}$	12
27	0.84-0.39	$\lambda_{crud} = 0.283 + 3.4 \cdot 10^{-3}T - 7.3 \cdot 10^{-7}T^2$	This work
31	1.53-0.54	$\lambda_{crud} = 2.1107 - 1.2 \cdot 10^{-3}T + 2.0 \cdot 10^{-7}T^2$	This work
40	1.1-0.4	$\lambda_{crud} = \{0.5 / [(1-p)\lambda_s + p\lambda_w] + 0.5 \cdot [(1-p)\lambda_s + p\lambda_w] T^{-1}\}^{-1}$	9

4. Conclusions

We have investigated thermal properties of cruds controlling porosity fabricated using sputtering system and simulated PWR primary loop in this work. All crud layer is a non-stoichiometric spinel nickel ferrite (Ni_{1-x}Fe_{2+x}O₄) in SEM-EDS observation. The porosity of crud was controlled from 22% to 31% by increasing heater temperature in the range of 345 $^{\circ}$ C to 355 $^{\circ}$ C. Thermal conductivity of crud decreases by 70% with increasing the porosity to 31%. Thermal conductivity of crud manufactured in this work decreased with increase in the temperature and it has a quadratic equation of temperature, unlike the results of previous other studies. It might be because the thermal conductivity of crud is multiply affected by other properties such as surface

structure and its thermal stability as well as its porosity. Therefore, it indicates that thermal conductivity of many types of cruds having various properties are measured to understand well the heat transport of crud for temperature.

Acknowledgments

This work was financially supported by the National Research Foundation of Korea (NRF) grant funded by the government of the Republic of Korea (RS-2022-00143316) and also by the Korea Hydro & Nuclear Power Co., Ltd. of the Republic of Korea (L24S013000).

REFERENCES

- [1] P. Millett, PWR Primary Water Chemistry Guideline, Rev. 4, Electric Power Research Institute, USA, Report EPRI TR-105714-V1R4, 1999.
- [2] J. Chen, On the Interaction between Fuel Crud and Water Chemistry in Nuclear Power Plants, SKI Report 00:5, 2000.
- [3] J. Deshon, PWR Axial Offset Anomaly (AOA) Guidelines, Rev. 1, EPRI Report, 1008102, EPRI, Palo Alto, 2004.
- [4] D. Hussey, D. Wells, Fuel Reliability Guidelines: PWR Fuel Cladding Corrosion and Crud, Rev. 1, EPRI Report, 3002002795, EPRI, Palo Alto, 2014.
- [5] J. Deshon, D. Hyssey, B. Kedrick, J. McGurk, J. Secker, and M. Short, Pressurized Water Reactor Fuel crud and corrosion modeling Nuclear Reactor Power Monitoring, Journal of Materials, 2011.
- [6] G. Wang, W.A. Byers, M.Y. Young, J. Deshon, Z. Karpitas, and R.L. Oelrich, Thermal conductivity measurements for simulated PWR crud, International Conference on Nuclear Engineering, 2013
- [7] J. S. Lee, G. Kim, Crud and Oxide Layer Modeling for Safety Analysis of a PWR, Trans. KNS Spring Meeting, Jeju, Korea, 2016.
- [8] J. S. Lee, KINS 의 설계기준사고 신안전기전 및 규제검증방법론 개발 현황, Nuclear Safety & Security Information Conf., Deajeon, Korea, 2019.
- [9] J. S. Lee, H. D. Jeong, Y. S. Bang, Thermal resistance effects of crud and oxide layers to the safety analysis, Topfuel, 2018.
- [10] N. Cinosi, I. Haq, M. Block, S.P. Walker, The effective thermal conductivity of crud and heat transfer from crud-coated PWR fuel, Nuclear Engineering and Design, 792-798, 2011.
- [11] F. C. Gunther, Photographic study of surface =boiling heat transfer to water with forced convection, Transactions of the ASME, 73, 115-123, 1951.
- [12] A.T. Nelson, J. T. White, D.A. Andersson, J.A. Aguiar, K.J. McClellan, D.D. Byler, M.P. Short and C.R. Stanek, Thermal expansion, heat capacity, and Thermal conductivity of Nickel ferrite (NiFe_2O_4), The American Ceramic Society 97, 1559-1565, 2014.