

Comparison of Chrome and Chrome Oxide Coating with CHF

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1. Introduction

The major interest of nuclear energy safety is to prevent the radioactive core's exposure due to meltdown or outer wall damage. During Fukushima accident, the fuel claddings were exposed to high temperature condition, causing Zirconium, the main component of cladding, to react with water. The oxidation of Zirconium produced hydrogen and this stacked up inside the dome until hydrogen explosion took place and radioactive materials were released. Consequently after Fukushima accident, interest grew upon the concept of accident-tolerant-fuel (ATF).

The major purpose of ATF is to show improved safety response during accidents while holding moderate normal operating conditions at the same time. There are 3 main directions of ATF: modification of current cladding, Zircaloy, aimed for further corrosion and oxidation resistance, trying different materials to replace Zircaloy, and changing the oxide fuel itself [1]. The most efficient way to implement in current nuclear power plants is improving Zircaloy's oxidation resistance, thus inhibiting further hydrogen release and many experiments were conducted comparing oxidation with various coating materials on Zircaloy surface. Amongst them Cr and SiC based coatings show excellent oxidation resistance in high temperature conditions, and in case of Cr coated Zircaloy-4, weight gain by oxidation decreased 75% compared to bare Zircaloy-4. Surface investigation with scanning electron microscope (SEM) indicates formation of chromia (Cr_2O_3) layer on the outermost surface and this chromia inhibits further oxidation and hydrogen embrittlement inwards [2]. But beside from good material properties, other factors like compatibility to formal design, thermodynamic limitations, and absorption neutron cross section accompanied with efficiency during normal operation condition should be considered before implementing the coating on to cladding surface. Especially critical heat flux (CHF) should be considered when modifying the cladding's surface since it is a criterion for temperature condition during normal operation and safety margin during accidents, meaning economics and safety response is directly related. Kam et al., evaluated SiC and Cr based coating's CHF, each coated with physical vapor deposition (PVD) sputtering and electroplating on SS surface, with pool boiling experiment. SiC had hydrophilic properties so wettability increase lead to CHF enhancement but Cr

had hydrophobic properties so CHF was 40% lower than bare SS plate's 1020 kW/m² [3].

Accepting that Cr has limitations regarding CHF, this study aims for measuring CHF of direct coating of chromia instead, which is the key of ATF concept that forms under high temperature oxidation condition. When SS or Cr is coated, chromia that forms from the outer rim protects not only cladding, but also the original coating so the required thickness becomes inefficient [4]. If chromia is somehow directly coated, it needs to only protect cladding and the required thickness would be much smaller so it is reasonable to try chromia instead of Cr. In this study chromia coatings were done by chromia nanofluid's boiling deposition upon Ni-Cr (80/20) wires and for comparison, Cr coated wires with DC sputtering and bare wires were also prepared. CHF measurements were performed by pool boiling experiment and surface investigation of test samples were done by contact angle measurements and SEM. In case of chromia coatings, samples were sorted by coating heat flux and duration time as variables to find optimum condition for maximum CHF. Cr coatings were sorted by different coating thickness.

2. Experimental Setup

2.1 Test specimen preparation

Chromia nanoparticle with particle size less than 100nm (Sigma-Aldrich) is used to form 0.01vol% chromia nanofluid with distilled (DI) water as base fluid. Stabilizing this suspension is required and it is done with sonication and modifying surface charge density of collide particles by controlling pH [5]. Stability of this suspension is assessed by zeta potential with Zeta Sizer (Malvern). Normally, when absolute value of zeta potential is over 30 mV, the suspension has moderate stability. The suspension is sonicated for 10 minutes and pH is modified to 10 by putting adequate amount of NaOH solution and 0.01 mol/L of NaCl powder is added just for the measurement as supporting electrolyte to reduce IR drop of the sample. Table I shows zeta potential measurement results and this indicates the modified suspension has sufficient stability.

Coating of Cr particle is done by DC sputtering. Usually, sputtering is done with metal surface or wafer since the particle deposition occurs in single direction. To coat the whole surface of Ni-Cr wire sputtering was done 2 times for all specimens, flipping the wire upside

down after first sputtering was over. The coating thickness was varied with 100, 300, and 500 nm.

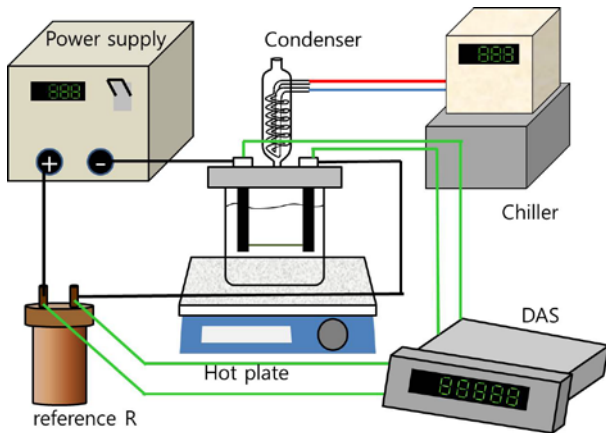


Fig. 1. Test apparatus

Table I: Zeta potential of chromia nanofluid (mV)

	pH 7	pH 10
Sample 1	-1.01	-33.2
Sample 2	-1.14	-31.3
Sample 3	-1.10	-35.8
Average	-1.08	-34.4

2.2 Experimental Apparatus

Experimental apparatus is as shown in Fig. 1. Glass basin is placed on hot plate and test specimen connects copper legs coated with Teflon. Diameter of the specimen wire is 0.5mm and the length is 55mm. 5kW DC power supply is used to control heat flux. Data acquisition system (DAS) records the voltage on the specimen and reference resistance of 0.001 Ω . From the voltage data of reference resistance, the current could be calculated and the power on the specimen is calculated by multiplying the current and the voltage on the specimen. Finally, heat flux is acquired by dividing the power with the total area of the wire, $8.64e-5 \text{ m}^2$. Base fluid's temperature is held constant at 100 $^{\circ}\text{C}$.

2.3 Experimental Procedure

Before coating, preliminary experiment for CHF measurement of chromia nanofluid is required. This is because nanofluid CHF enhancement is directly linked with particle deposition on the heated surface, which is the coating mechanism of boiling deposition. Average CHF of chromia nanoparticle was 2010 kW/m^2 .

If wire is coated by boiling deposition, heat flux on the specimen and coating duration time could be major variables that can possibly affect the result of coating. Studies indicate the surface is coated better at higher heat flux. Also, when the boiling deposition time is too short, the coating would be imperfect, causing partial CHF. When coating time range is short enough, there was proportional CHF increase with increasing time [6]. If coating time is long enough, the wire has saturated

coating and this wire possibly has maximum CHF. Thus in order to get maximum CHF by coating, variables of heat flux condition and coating time should be specified. Setting chromia nanofluid's CHF of 2010 kW/m^2 as standard, heat flux condition were varied as 40, 60, and 80% of the standard. After testing those conditions under 20 minutes of coating, heat flux showing maximum value of CHF is again specified with coating time of 20, 40, and 60 minutes.

Apart from CHF measurement with wire pool boiling, surface investigation with SEM (Fig. 2), contact angle with $12\mu\text{m}$ droplet (Fig. 3, Table II), and capillary wicking height (Fig. 4) is measured to help to understand the CHF results..

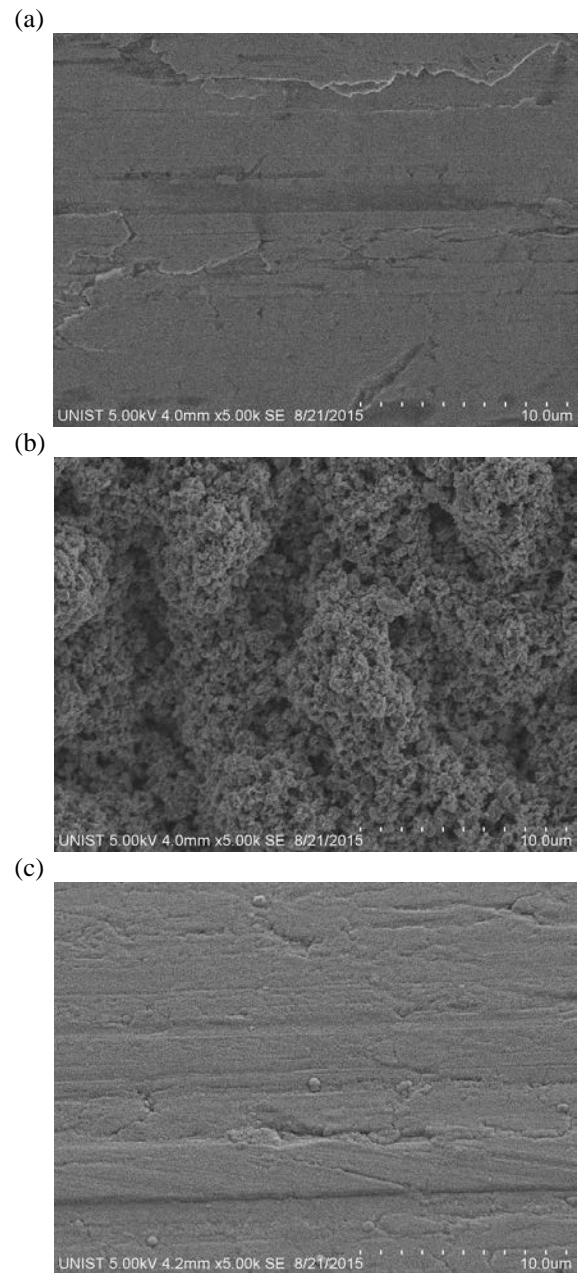


Fig. 2. SEM image of (a) bare wire, (b) chromia coating, and (c) chrome coating

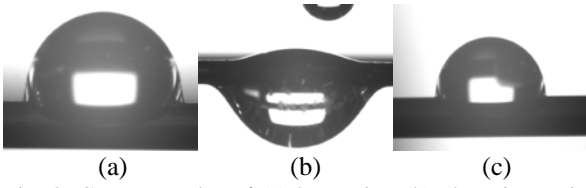


Fig. 3. Contact angles of (a) bare wire, (b) chromia coating, and (c) chrome coating

Table II: Contact angles

Coatings	Bare	Chromia	Cr
Angle(°)	79.91	16.61	89.42

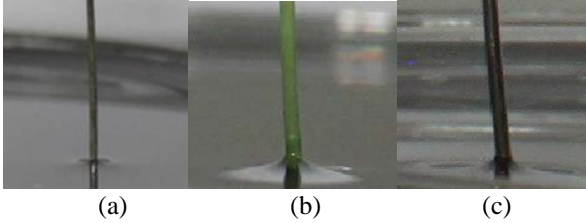


Fig. 4. Capillary length of (a) bare wire, (b) chromia coating, and (c) chrome coating

3. Results and Discussion

Test results are summarized in Table III and Fig. 5. Chromia coated wires show enhanced CHF, almost twice compared to bare wire. Cr, on the other hand, shows slight decrease and this indicates chromia coating is better in terms of CHF than Cr coating.

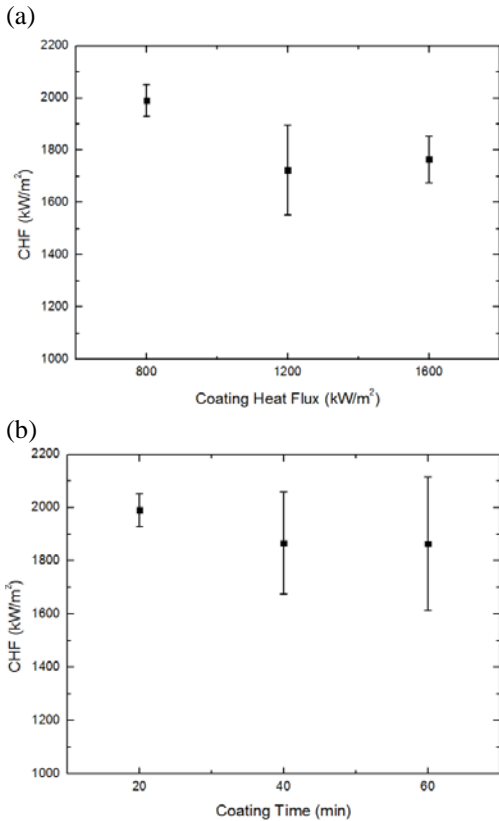


Fig. 5. CHF of chromia coated wire: (a) heat flux variation, (b) coating time variation

Table III: CHF results of test samples (kW/m²)

	Sample 1	Sample 2	Sample 3	Average
Bare	1088	969	1104	1054
Cr 100nm	1066	986	1042	1031
Cr 300nm	1044	957	1041	1014
Cr 500nm	942	993	946	960
Chromia 40%, (800kW/m ²), 20 min	1929	2030	2012	1990
Chromia 40%, 40 min	2001	1916	1675	1867
Chromia 40%, 60 min	1985	1613	1996	1864
Chromia 60% (800kW/m ²), 20 min	1570	1707	1896	1724
Chromia 80% (800kW/m ²), 20 min	1854	1711	1730	1765

3.1 Optimized coating condition

Results indicate that there was not much difference when the heat flux is varied. The reason why maximum heat flux had no effect could be different time scale and experiment methods. In the case of TiO₂ nanofluid study, time scales are relatively short compared to 20 minutes when heat flux is controlled [6]. Coating duration time could vary since the increasing rate was fixed with 400 kW/m²/min. This mean higher heat flux had longer coating time so the CHF increase was not solely dependent on heat flux. There was no difference when time steps were varied indicating the coating reached saturation point after 20 minutes. In case of Cr coating, there was no noticeable difference between CHF values when the coating thickness was varied.

3.2 CHF enhancement mechanism

As anticipated from chromia nanofluid's CHF, the coated wires also showed excellent enhancement. CHF enhancement due to wettability increase is widely known since hydrophilic traits of surface can delay vapor film or dry spots that are prelude to CHF. Kandlikar emphasized the importance of wettability by modifying Zuber's CHF model (Eqs. (1)), putting receding contact angle as variable and it is written as Eqs. (2) [7, 8].

$$q_z^* = \frac{\pi}{24} h_{fg} \rho_g^{1/2} [\sigma g (\rho_f - \rho_g)]^{1/4} \quad (1)$$

$$q_c^* = h_{fg} \rho_g^{1/2} \left(\frac{1 + \cos \beta}{16} \right) \left[\frac{2}{\pi} + \frac{\pi}{4} (1 + \cos \beta) \cos \phi \right]^{1/2} \times [\sigma g (\rho_f - \rho_g)]^{1/4} \quad (2)$$

Assuming that Zuber's CHF model (Eqs. 2) is the case of bare wire's CHF of 1104 kW/m², other coefficient values are obtained and assuming the measured angles are close with receding contact angle, theoretic calculation according to measured angle and experimental values were compared in Fig 6. The model

predicts 1.97 times increase when the contact angle changed from 79.91 to 16.61 degrees and this is similar with 1.89 times increase of experimental data. Decrease ratio of Cr CHF is also similar as model predicts 19% decrease while experimental data shows 14% decrease.

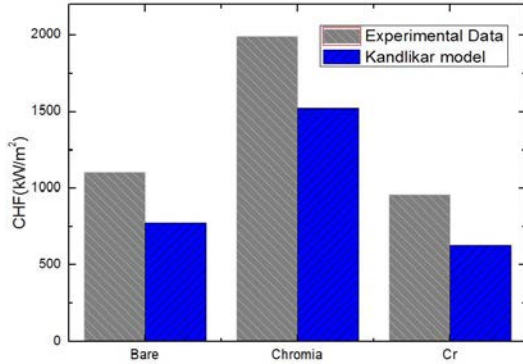


Fig. 6. Comparison between experimental value and Kandlikar model

Porous structure also plays role in delaying CHF by securing physical path for fluid when the pore is hydrophilic [9]. Fig. 2 shows that chromia coated surface is much more porous compared to bare wire and Cr coated wires. This is induced by different coating method since PVD does not form porous structures while nanofluid boiling deposition results higher porosity due to its irregular coating density. However, even if Cr surface had porosity, hydrophobic pores of Cr could further damage CHF [9]. Capillary length showed no wicking for Cr and bare wire, only chromia coating showed height of 0.9mm.

4. Conclusions

Following results were obtained.

- (1) Chromia coating obtained by boiling deposition enhances CHF up to 2030 kW/m², while Cr shows slightly negative CHF value compared with bare wire.
- (2) Chromia coating variation by heat flux and coating time condition is insignificant. Cr coating also had little relation with coating thickness.
- (3) CHF enhancement could be explained from capillary wicking, porous structure and wettability increase.

CHF analysis showed favorable results for chromia compared to chrome.

REFERENCES

- [1] S.J. Zinkle, K.A. Terrani, J.C. Gehin, and L.L. Snead, Accident tolerant fuels for LWRs: A perspective, *Journal of Nuclear Materials*, Vol. 448, pp 374-379, 2014.
- [2] J.C. Brachet, M. Le Saux, T. Guillbert, S. Urvoy, E. Rouesne, M. Le Flem, I. Idarraga-Trujillo, F. Schuster, F. Lomello, A. Billard, E. Monsifrot, G. Velisa, J. Bischoff, and A. Ambard, Chromium coated nuclear fuel claddings for enhanced accident tolerant LWRs fuel, IAEA Technical Meeting on "Accident Tolerant Fuel Concepts for LWRs", TN, USA, 13-17 October, 2014.

- [3] G.H. Seo, H.H. Son, U.J. Jeong, G.D. Jeun, and S.J. Kim, Pool boiling heat transfer characteristics of chromium coatings deposited by RF magnetron sputtering, *Transactions of the Korean Nuclear Society Spring Meeting*, Jeju, Korea, 7-8 May, 2015.

- [4] K.A. Terrani, C.M. Parish, D.W. Shin, and B.A. Pint, Protection of zirconium by alumina- and chromia- forming iron alloys under high-temperature steam exposure, *Journal of Nuclear Materials*, Vol. 438, pp. 64-71, 2013.

- [5] I. Ostolska and M. Wisniewska, Investigation of the colloidal Cr₂O₃ removal possibilities from aqueous solution using the ionic polyamino acid block copolymers, *Journal of Hazardous Materials*, Vol. 290, pp. 69-77, 2015.

- [6] H.D. Kim, E.H. Kim, and M.H. Kim, Effect of nanoparticle deposit layer properties on pool boiling critical heat flux of water from a thin wire, *International Journal of Heat and Mass Transfer*, Vol. 69, pp. 164-172, 2014.

- [7] S.G. Kandlikar, A theoretical model to predict pool boiling CHF incorporating effects of contact angle and orientation, *Journal of Heat Transfer*, Vol. 123, pp. 1071-1079, 2001.

- [8] N. Zuber, Hydrodynamic aspects of boiling heat transfer, Ph.D. Thesis, Univ. of California, 1959.

- [9] O'Hanley, C. Coyle, J. Buongiorno, T. McKrell, L.W. Hu, M. Rubner, and R. Cohen, Separate effects of surface roughness, wettability, and porosity on the boiling critical heat flux, *Applied Physics Letters*, Vol. 103, pp. 1229-1242, 2013.