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Evaluation Wettability of nanofluid on the Surface of Zircalloy 4 Before and after Oxidation

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Abstract. The solid surface tension plays an important role in the heat and mass transfer system for heat exchanger equipment. In the nuclear power plant industry, Zircalloy 4 has been used for long time as structure materials. The purpose of the experimental is to study solid state surface tension behavior by measure contact angle of aquades and Nano fluid contain nano particle alumina on metal surface of Zircalloy 4 before and after oxidation at 700o C by sessile drop method. The experiment is to measure the static contact angle and drop of aquades and nano fluid contains nano particle alumina on zircalloy 4 with different spreading time from 1 to 30 minute. It was observed that zircalloy 4 after oxidation lose their hydrophobic properties with increasing elapsed time during drop of a aquades and nano fluid on the surface of alloy compared with zircalloy 4 before oxidation. As a result the contact angle of aquades and nano fluid on surface of zircalloy 4 before and after oxidation is decrease grdually during increasing elapsed time. While the magnitude diameter drops of aquades and nano fluid and wetting surface are increase with increasing elapsed time on the surface of Zircalloy 4 before and after oxidation. It was observed that oxidised zircalloy4 good wettability properties compare with non oxidised zircaloy 4.

Keywords: zircalloy 4,contact angle,nanofluid,wettability,oxidised

1. Introduction

Zirconium alloys such as zircalloy 1,2,3,4 , zirlo, excel, and ZrNb alloys are used in nuclear industries due to of their low neutron cross section absorption and their excellent mechanical and corrosion properties. The application of zircaloy-4 with Zr-1.5%Sn-0.2%Fe-0.1%Cr. alloying element in the alloy is used for pressurized water reactors (PWR) nuclear power plant. The zircalloy 4 is used for structural material of nuclear fuel rod for cladding, control rod guide tubes, and grid spacers. (1,2). During accident such as loss of Flowing Accident (LOFA) and loss of Coolant accident (LOCA), fuel rods made of a zirconium alloy were oxidized at high temperatures producing H gas that leading to the core underwent degradation and then directly to meltdown. Currently, the nuclear community tried to evaluate and improve fuel systems with the main purpose to preventing and mitigating possible deleterious effects in nuclear fuel materials under high risk accident [3,4]. One of the methods to improved performance of zirconium alloy is to modified zirconium alloys by alloying [5]. The other method to improve zirconium alloy is used multiple coating with excellent corrosion resistance, chemical inertness [6,7]. Unfortunately, their applicability of ceramic material is limited due to low ductility, low heat transfer and crack resistance. The second method to mitigating structural nuclear materials meltdown during LOCA is to use nanofluid as emergency core cooling system (ECCS) media during accident. Nanofluid is suspension of nano particles in a base fluid. The properties of nanofluid are improved the heat transfer coefficient and conductivity compared with the original base fluid. These nano particles usually metal or metal oxide, increase the conduction and convection coefficients of base fluid (8). The studies of nanofluid for nuclear power plants application such as secondary cooling system and emergency core cooling system (ECCSs) should be compatible with conventional systems during normal operations to make nanofluid technologies practical in Nuclear Power Plants. One of the methods to evaluation performance nanofluid as media cooling system is wettability. Wettability can be defined as interaction of a fluid with a solid surface of material such as metal. The wetting phenomena plays an important role in the mass and heat transfer for engineering structure such as heat exchanger, steam generation, waste heat recovery and emergency cooling system. An index of wetting properties is defined by the magnitude of contact angle between the liquid and solid surface of metal (9, 10). Solid metal provides planar surface that allow the geometric measurement of a contact angle on the metal. If the contact angle is lower than 90^o the material is hydrophilic otherwise it is hydrophobic.

The zircalloy 4 as an engineering material is used as nuclear material structure in the primary cooling system. The nominal chemical composition of Zircaloy-4 is Zr e 1.5 wt%Sn e0.2 wt%Fe e 0.1 wt%Cr [(11). The contact angle is highly influenced by surface finish composition of the metal and nanofluids. Contact angle nanofluid and solid of zircalloy 4 before and after oxidation in nanofluids media contain nanoparticle alumina is rarely studied. During LOCA accident the surface of zircaloy 4 is covered by oxide layer ZrO2 due to oxidation zircalloy 4 by atmosphere. The purpose of the present study is to examine the contact angle of aquades contain nanoparticle alumina on the metal surface of zircalloy 4 before and after oxidation at 700^{o}C to form oxide layer ZrO2 with different spreading time will be studied. The present study is to evaluate wettability behavior of nanofluid contain 0,01 gpl nanoparticle alumina on surface of zircalloy 4 before and after oxidation by using a sessile drop methods.

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2. Experimental

2.1. Material and nanofluid

The specimens used in this experiments were circular discs of zircalloy 4 having 1 Cm in diameter and 3 mm in thickness. Figure 1 showed specimens a) before oxidation and b) after oxidation at 700^{o}C in air furnace. The specimen is zircalloy 4 with the major chemical composition (in wt%) 98%Zr, 1,4Sn, 0.24Fe 0.15Cr. The specimens were roughed by wet grinding with different emery paper 230,500, 800 and finished at1000 grit, degreased with detergent after that cleaned with ultrasonic cleaner in alcohol solution. In the present study, Al_2O_3 was used as nanoparticles. Al_2O_3 nanoparticle from Inframat with purity 99.99, surface area (BET) 201 m^2/g and the average primary particle size 20nm. Figure 2 showed nanoparticle of Al_2O_3 examination by TEM with magnificiant of 20 nm. It can be seen that the shape of the particles were approximately rounded. The base fluid of aquades was used for this experiment. Nanofluid is produced by mixing of aquades with 0.01 gpl Al_2O_3 nanoparticles. The nanofluids were prepared by incorporating 0.01 gram of Al_2O_3 nanoparticles mixed into 1 L aquades and mixed by magnetit stirrer for 30 minutes. After mixing, ultrasonic vibrator operating at a frequency of 44 kHz was used to stabilise nanofluid for 30 min in order to the Al_2O_3 particles were dispersed and stabilized in aquades [12].

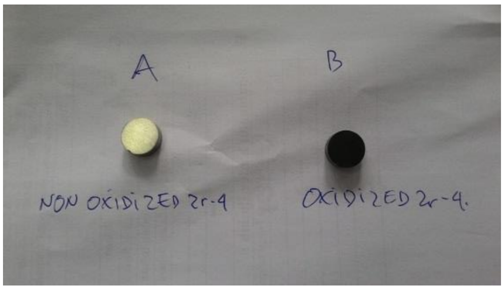

Figure 1. Specimens a) before and b) after oxidation

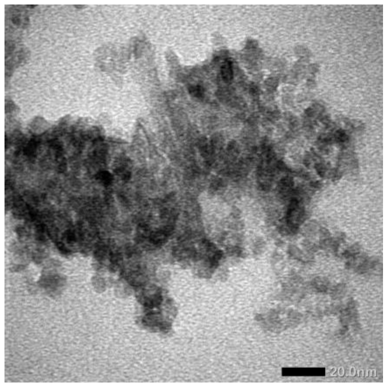

Figure 2. Nanoparticle Al_2O_3 examination by TEM with magnificiant of 20 nm

2.2. Sessile drop measurement

The wettability characteristics of nanofluid on the surface of the zircalloy 4 were carried out to evaluate contact angle measurement. The contact angle can be defined as the angle between the liquid phases formed on the surface of a stainless steel and the line tangent to the droplet radius from the point of contact with the surface of stainless steel. The Contact angle perform have been conducted by sessile drop method (13) equipment system from Kruss GmbH goniometer with a resolution of 0.1^o in the measuring range of 1-180^o. This equipment has been provided by software drop shape analysis (DSA 4) for controlling the experiment and analyzing the drop shape to calculate the contact angle. Droplets of known volume of 2 μL were dropped on a substrate of zircalloy 4 before after oxidation using an automatic dispenser and injected slowly onto the solid surface by a syringe. The experiments were conducted under similar air conditioned laboratory environments. The measured values of the contact angle, the images of the droplets were taken directly after 20 second deposition in order to eliminate the impact of droplet evaporation. The contact angle tests were conducted at an ambient temperature of 27 ^{o}C.

2.3. Sample characterization
Surface morphology of the zircalloy 4 before and after oxidation was examined by using an optical microscopy.

3. Results and discussion

3.1. Optical image and x ray diffraction of zircalloy 4 before and after oxidation
Figure 3(a) and (b) shows surface morphology of the zircalloy 4 before and after oxidation that was examined by using an optical microscope. Surfaces morphology of the sample relative the same roughness was produced by wet grinding of zircalloy 4. The color of oxidized zircalloy 4 relatively different with non-oxidized zircalloy 4 due to oxide scale was formed on the zircalloy 4 during oxidation of zircalloy at 700 ^{o}C. This is agreement with the Reif [14]. Oxidation of zircalloy at 600 and 700^{o}C in air furnace resulted thin of oxide scale of zirconium oxide. Reaction zirconium with oxygen resulted ZrO2 [15].

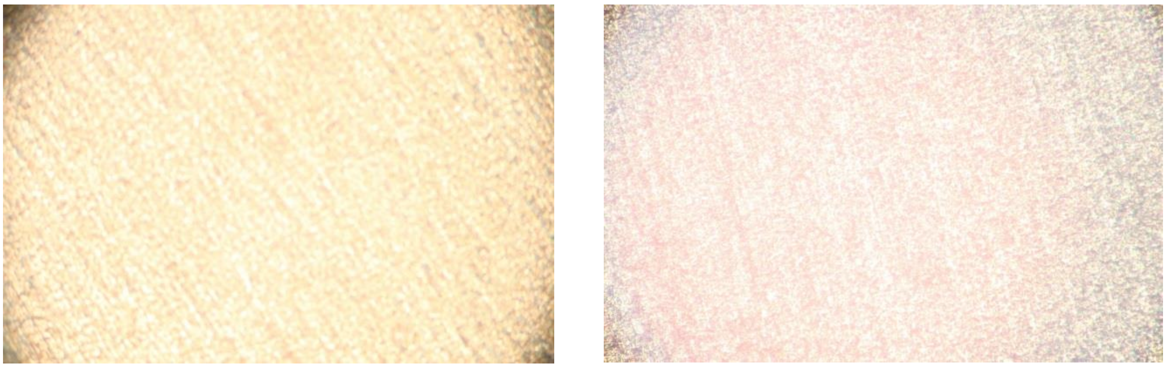
(a) (b)

Figure 3. Surface morphology of zircalloy4 a) before and b) after oxidation

3.2. Effect of spreading time on the wettability aquades and nanofluid on the surface of oxidized and non-oxidized Zircalloy 4
Dynamic wetting behavior was evaluated through measuring contact angles between aquadest and nanofluid epoxy and oxidized zirconium alloy and non-oxidized zirconium alloy as shown In Figure 4(a) and (b). From this figure depicted the contact angle of droplet aquadest and nanofluid on zircalloy 4 before and after oxidation as a function of spreading time multiple measurements. From Figure 4(a) and (b) , generally it can be noted that the contact angle value of aquadest and nanofluid on the surface of non-oxidized zircalloy 4 are higher compare with oxidized zircalloy 4 at different spreading time. From figure 4(a), it is shown that at early-stage spreading time, the contact angle of aquades were not different significantly on the surface of non-oxidized zircalloy 4 and oxidized zircalloy 4 . After 30 second elapsed time, the contact angle of aquadest on the surface of non-oxidized zircalloy 4 and oxidized zircalloy 4 was different significantly. The contact angle of aqueduct 66^{o} on non-oxidized zircalloy 4 and the contact angle were decreased gradually with elapsed time. Finally, the contact angle was reach 42^{o} and there was a decreased of 24° on the contact angles. Contact angle of aqueduct on surface of oxidized zircalloy 4 is described in figures 4(a). In the first spreading time, the contact angle of aquadest 64^{o} on oxidized zircalloy 4 and the contact angle were decreased significantly during elapsed time. At the end elapsed time, the contact angle was reach 42^{o} and there was a decreased of 24° on the contact angles. It can be concluded that contact angle of aquadest on the surface of oxidized zircalloy 4 lower compared with non-oxidized zircalloy 4.

Figure 4(b), depicted shown that at early stage spreading time, the contact angle of nanofluid were different significantly on the surface of non-oxidized zircalloy 4 and oxidized zircalloy 4. After 30 second elapsed time, the contact angle of nanofluid on the surface of non-oxidized zircalloy 4 and oxidized zircalloy 4 was big different. Initially, the contact angle of nanofluid 86º on non-oxidized zircalloy 4 and the contact angle were decreased gradually with elapsed time. Finally, the contact angle was reach 44º and there was a decreased of 42◦ on the contact angles. Contact angle of nanofluid on the surface of oxidized zircalloy 4 is described in figures 4(b). At the initial of spreading time, the contact angle of nanofluid 79º on oxidized zircalloy 4 and the contact angle were gradually decreased significantly during elapsed time. At the end elapsed time, the contact angle was reach 28º and there was a decreased of 31˚ on the contact angles. It suggested that the wettability of nanofluid on the oxidized zircalloy 4 became improved than that of non-oxidized zircalloy 4. The evident showed that the decrease of contact angle of oxidized zircalloy indicated dramatic changes the contact conditions due to chemistry behavior of surface zirconium alloy 4. According to Refs. [16, 17], there was a thin oxide film produced on the surface of sample that change behavior of wettability of nanofluid in the surface of oxidized zircalloy 4.

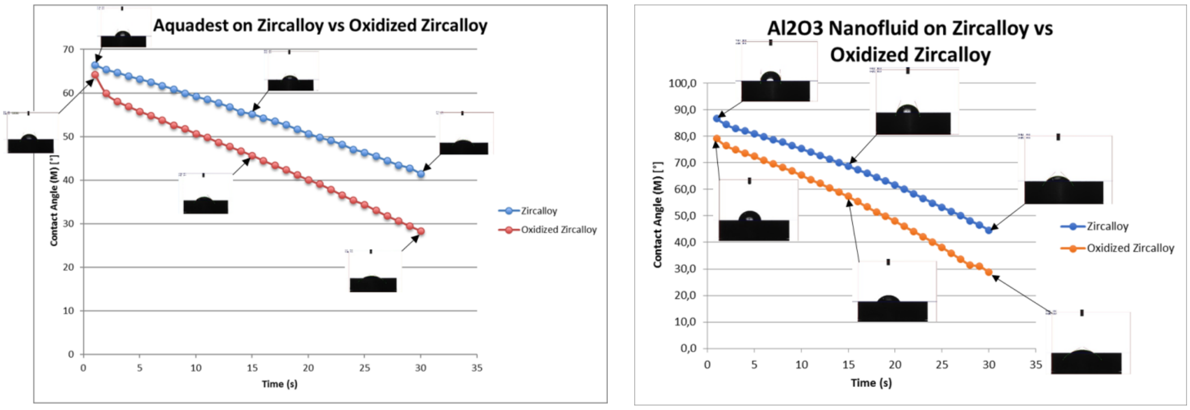

Figure 4. Measurements at ambient temperature of the spreading time of Zircalloy and Zircalloy oxidized on a) aquadest and b) nanofluid

The droplet image of aquadest and nanofluid on Zircalloy 4 before and after oxidation has been measured by using the sessile drop method is represented in Fig. 5 and 6 respectively. Generally, it is showed that the typical images of droplet at 0, 10,20 and 30s of aquadest and nanofluid on the surface of zirconium alloy 4 before and after oxidation are raise in diameter and contact angle decrease for longer spreading time. From figure 5, it is shown that at the early-stage spreading the liquid drop of low-viscosity aquades are different significantly on the surface of zircalloy 4 before and after oxidation. Fig.5(a) depicted the droplet of aquadest at 0,10,20, and 30s on the surface of zirconium alloy before oxidation. For long spreading time, the wetted area is found to grow and diameter of droplet increases while the contact angle is decrease significantly. The droplet of aquadest at 0, 10,20 and 30 minutes on zircalloy after oxidation showed in Figure 5(b). It can be seen that the wetting area of aquadest on the surface of zircalloy 4 after oxidation are more wide and contact angle relative small compare with zircalloy before oxidation. It can be concluded that wettability of aquadest on the surface of zirconium alloy after oxidation are considered good wettability's compare with zirconium alloy before oxidation.

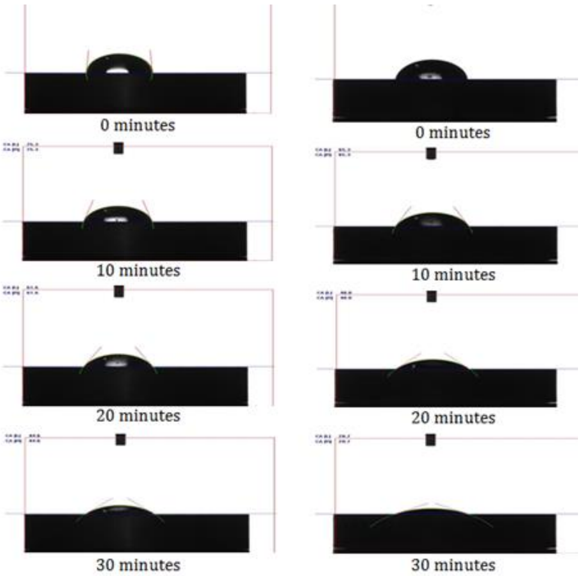

Figure 5. A droplet of aquadest on the surface of Zircalloy 4 a)before and b)after oxidation

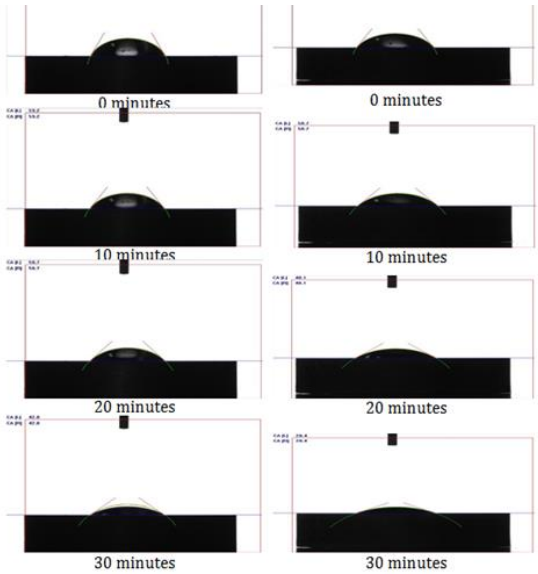

Figure 6. A droplet of nanofluid on the surface of Zircalloy 4 a) before and b)after oxidation

Figure 6 (a) and (b) depicted the different of the droplet image at 0, 10, 20 and 30 minutes of nanofluid on the surface of zircalloy 4 before and after oxidation, respectively. From figure 6, it is shown that at the early-stage spreading (0 minute) the liquid drop of nanofluid on the surface of zircalloy 4 before oxidation is different significantly with zircalloy 4 after oxidation. The droplet of nanofluid on the surface of zircalloy 4 after oxidation show semicircle with long diameter and small contact angle compared with zircalloy 4 before oxidation. A partially wetting on the substrate appeared on the surface of zircalloy 4 before oxidation. For long spreading time, the wetted area is developing and the diameter of droplet increase while contact angle decrease for wettability's of nanofluid on the surface of zircalloy 4 before and after oxidation. The droplet size of nanofluid on the surface of zircalloy 4 after oxidation shows wide diameter compared with zircalloy 4 before oxidation. For long spreading time, the contact angle of nanofluid on the surface of zircalloy 4 after oxidation is small compared with zircalloy 4 before oxidation. It can be concluded that wettability's of nanofluid show good performance on the surface of zircalloy 4 after oxidation compare with zircalloy 4 before oxidation. The perf romance of nanofluid on surface of zircalloy 4 after oxidation shows good wettability properties due to the function of oxide scale zirconium oxide on the surface of zircalloy 4 [18] .

4. Conclusion

The wettability behavior of aquadest and nanofluids contains 0.01 gpl nanoparticle alumina on the surface of zircalloy 4 before and after oxidation samples were studied using sessile drop methods. The results obtained can be summarized as follows:

(i) The values of contact angle decrease gradually with increasing spreading time.
(ii) The diameter of droplet of aquadest and nanofluid increase with increasing spreading time.
(iii) The wettability of the aquadest and nanofluid on surface of the oxidized zircalloy 4 are better compared with non-oxidized zircalloy 4.

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References

[1] H.L. Yang , Y. Matsukawa , S. Kano, Z.G. Duan , K. Murakami, H. Abe, 2016, Journal of Nuclear Materials 481, p. 117-124
[2] H.L. Yang, S. Kano, Y.Matsukawa , Y.F. Li , J.J. Shen, F. Li, Z.S. Zhao, Y. Satoh, H. Abe,2016, Materials and Design 104,p. 355–364
[3] M. Steinbrück ⥣, M. Böttcher, ,2011,Journal of Nuclear Materials 414 p. 276–285
[4] É. V. Li, M. V. Koteneva, S. A. Nikulin, A. B. Rozhnov, and V. A. Belov,2015 Metal Science and Heat Treatment, 57, Nos. 3 – 4, p.215
[5] Li Nie, Yongzhong Zhan ⥣, Tong Hu, Xiaoxian Chen, Chenghui Wang 2013,Journal of Nuclear Materials 442, p.100–105
[6] K. Sridharan, S.P. Harrington, A.K. Johnson, J.R. Licht, M.H. Anderson, T.R. Allen, Mater. Des. 28 (2007) p.1177-1185
[7] A.S. Kuprin et all, 2015,Journal of Nuclear Materials,p 400-406
[8] Albadr J, Tayal S, Alasadi M, 2013, Thermal Engineering 1, p38–44
[9] Koen G. Winkels, Joost H. Weijs, Antonin Eddi, and Jacco H. Snoeijer, 2012,, PHYSICAL REVIEW E 85,,055301
[10] Belaud V, et al, 2015, Tribological International, 82, p343–349
[11] Vivian S. Tong, T. Ben Britton, 2017 Acta Materialia 129,p 510-520
[12] Djoko Hadi Prajitno and Dani Gustaman Syarif, 2015, Conference Series: Materials Science and Engineering 214 (1), 012015
[13] Prajitno D H and Syarif D G, 2016, Journal of Physics: Conference Series 739 012029
[14] M. Reif, F. Scherm, M. C. Galetz, U. Glatzel, 2014,Oxidation of Metals 82.,p. 99-112
[15] O. Coindreau, C. Duriez, S. Ederli, 2010, , Journal of Nuclear Materials 405, p.207–215
[16] Aiguo Feng a, Benjamin J. McCoy a, Zuhair A. Munir a,*, Domenick Cagliostro, 1998,Materials Science and Engineering A242 p 50
[17] Jiangyou Long, Minlin Zhonga, Peixun Fan, Dingwei Gong, and Hongjun Zhang, 2015,Journal of Laser Applications 27, S29107
[18] P. Tsai, R. C. A. van der Veen, M. van de Raa, and D. Lohse, 2010, Langmuir 26, p. 055301-1-055301-4