The Effect of Mo addition in stainless steels on the corrosion behavior in the nano fluids contain Al2O3 nano particles

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Abstract. The effects of molybdenum in stainless steel on the corrosion behaviour in nano fluids contain nano particle Al2O3 in the de mineralized water have been investigated. Open circuit potential (OCP), Tafel polarization and electrochemical impedance spectroscopy (EIS) testing was performed in the demineralized water contain nano particle 0, 01% Al2O3 as Nano fluid. Metallurgical techniques such as X-ray diffraction (XRD) and optical microscopy were used to characterize the alloys before and after corrosion testing. According to the open circuit potential measurement of the stainless steel in the de mineralized water and nano fluid media, it is showed that stainless steel with Mo showed more negative OCP compared without Mo stainless steel. The results of the Tafel polarization technique show that corrosion currents stainless steels in the nano fluid decrease with the increasing of Mo content in the stainless steel. Surface morphology of the specimens by optical microscope examination showed that microstructure of stainless steel SS 304 and SS 316 alloys relatively unchanged before and after corrosion testing nano fluids. X ray diffraction examination of stainless steel with and without Mo after corrosion testing depict that γFe is major phase without oxide phase on the surface of alloy

1. Introduction
Nano fluids are a mixture of nano particles in a base fluid in the form colloidal. The properties of nano fluids are significantly improvement the heat transfer and conductivity characteristics from the original base fluid [1]. These nano particles usually a metal or metal oxide is increase conduction and convection coefficients behaviour of base fluid. Experimental studies on nanofluid single-phase heat transfer have been reported in the literature [2, 3]. Alumina-water and titania-water nanofluid are studies in turbulent convective heat transfer in tubes. Laminar convective heat transfer and viscous pressure loss of alumina–water and zirconia–water nanofluid are also having been studies. The studies of nanofluid for nuclear power plants application such as primary and secondary cooling system and emergency core cooling systems(ECCSs) were carried out by a number researcher [4,5] This studies were characterized by the improvement of critical heat flux (CHF) of nanofluid after injection in experiment of loss of coolant accidents (LOCAs). The benefits of nanofluid during simulation accident conditions show good results. It is clear that the nanofluid engineered ECCSs should be compatible with conventional systems during normal operations to make nanofluid technologies practical in Nuclear Power Plants [6].

Stainless steel shows very good corrosion resistance in various media because of its ability to form a thin protective passive film when its expose to environment [7]. The alloy 304 SS is austenitic steel with its properties non-magnetic, contain ii nickel, iron, carbon and at least 18% of chromium. The chromium element is responsible for the corrosion resistance of these alloys is attributed to the presence of a thin invisible passive film of Cr2O3 [8]. Tafel polarization technique has been used to
study this corrosion behaviour of metal in various media. But the adopted scan rates in the literatures vary from 0, 5 to 115 mV/s, and there are few instances of research work about the effect of scan rate on the Tafel polarization curve. In this paper, the corrosion behaviour of stainless steel 304 in nanofluid solution will be studied to illustrate how the Tafel polarization curve is disturbed by the charging current, the corrosion of stainless steel in nanofluid media contain nanoparticle ZrO2 is infrequently studied. The present work is to investigate the corrosion behaviour of stainless steel SS 304 and 316 in nanofluid solution contain 0,01 gpl nanoparticle Al2O3, by open circuit potential and potentiodynamic measurements, electrochemical impedance spectroscopy (EIS). The surface morphology of the samples is observed by optical microscopy, scanning electron microscopy (SEM) and By X-ray diffraction.

2. Experimental

2.1. Material and nanofluid

The specimens used in this experiments were circular discs stainless steel having 1.6 Cm in diameter and 2 mm in thickness. The specimens is stainless steel 304 and 316 with the major chemical composition (in wt%) 17,29 % Cr, 7,17% Ni, 0,39% Si, 0,56% Mn, 0%Mo, 0,066% C balanced Fe and 16,39 % Cr, 8,54% Ni, 0,39% Si, 0,5% Mn, 2,14%Mn, 0,02% C balanced respectively. The specimen was wet abraded with 500, 800 and 1200 emery paper, degreased with detergent after that cleaned with ultrasonic cleaner in alcohol solution [8].

Aqua demineralized water (adm) and 0.01 gpl Al2O3 nanoparticle were used to produce nanofluid. The Al2O3 nanoparticles were supplied by the inframat Advanced Materials. The nanofluid were prepared by incorporating 0,01 gram of Al2O3 nanoparticles with an average particle size of 30-60 nm mixed into 1 L aqua demineralized water by magnetite stirrer for 30 minute. After magnetite stirrer then an ultrasonic vibrator operating at a frequency of 44 kHz was used to mixing for 20 min in order to the Al2O3 particles were dispersed and stabilized in demineralized water. Nanoparticle and nanofluid preparation were described in [9].The Al2O3 nanofluid was then used for corrosion testing. Characterization of nanoparticle Al2O3 by TEM shown in Figure1.

2.2. Electrochemical study

Electrochemical tests were performed using corrosion cell. Electrochemical experiments were conducted in three electrode cell, a stainless steels disk as the working electrode, a saturated calomel electrode (SCE) as reference electrode and platinum wire were used as an auxiliary electrode. The experiments were recorded using an apparatus PCI4, G300 Gamry Potentiostat Instrument [10] connected to a personal computer provide with DC 105 software from Gamry [11]. Tafel polarization curve were obtained by the polarization of working electrode from cathodic to anodic direction at a scan rate of 5 mVS-1 and the data were analyzed using software Gamry Echem Analyst version 5.66.

2.3. Sample characterization

Corroded and no corroded samples were analysed by x ray diffraction (XRD) for phase present analysed XRD measurements were performed by using a Pan Analytical diffractometer equipped with a Cukα radiation source (1,5406A°). The scanning, 2θ region ranged from 30 to100. Optical Tables should have only horizontal rules and no vertical ones. Generally, only three rules should be used: one at the top of the table, one at the bottom, and one to separate the entries from the column headings. Table rules should be 0.5 points wide.

3. Results and discussion

3.1. Micrograph nanoparticle Al2O3

Figure 1 shows micrograph image of nanoparticle Al2O3 characterization by TEM. The image shows that the average of nanoparticle size approximately 5-20 nanometer.
3.2 Open Circuit Potential (OCP)

Figure 2 shows the variation of open circuit potential (OCP) with immersion time of stainless steel SS 304 and SS 316 alloys in adm+0.01gpl Al2O3 nanoparticle at the room temperature for 600 seconds. Basically, at the first time, OCP decreases rapidly for 50S periods after that the OCP increase gradually with lower slope for long time immersion. The OCP value of SS 304 at the first time then decreases to -97 Vs (SCE) for 50s. After that the variation of OCP with immersion time are increases slowly to 600s finish. The OCP value of SS 316 start -45 then decreases to -123 Vs (SCE) for 75s, and then, the variation of OCP with time are increase slowly until 600s. This indicates that the open circuit potential of stainless steel in nanofluid is actively drop for first time due to equilibrium during 50s then the OCP of stainless steel increases slowly with time until 50s finish as a result the stainless steels corroded before stable protective film took place to the entire surface of alloys.

3.3 Potentiodynamic polarization curves

Figure 3 depicted the cathodic and anodic polarization curves for SS 304 and 316 SS alloys immersed in nanofluid solution. The corrosion potential, polarization curves behavior and the plateau in the anodic and cathodic polarization of the SS 304 and 316 is dependent on the molybdenum content in the alloy [1].

The corrosion potential, corrosion current (icorr), corrosion rate, anodic and cathodic Tafel slope were calculated by the extrapolation of the logarithmic section of the anodic and cathodic Tafel line to the point of intersection. With it of the software DC corrosion 105, the results of Tafel anodic, cathodic slope and corrosion current, corrosion rate for stainless steel with and without molybdenum are calculated and tabulated in table 1. In table 1 it can be seen that the increase of molybdenum in the alloy SS 316 makes the anodic Tafel slopes and corrosion rate will decreasing. Anodic Tafel slope
value for SS 304 and 316 were 0.769 Vdec-1 and 0.327 Vdec-1, respectively. Cathodic Tafel slope value for SS 304 and 316 were 0.279 Vdec-1 and 0.171 Vdec-1, respectively. The distortion of the anodic slope can lead to the electrode process oxidation of stainless steel. The corrosion potential of SS 316 alloy in the nanofluid is -176 mv compared than for AISI 304 -148 mv. The higher corrosion potential of Stainless Steel 304 compared with SS 316 due to SS 304 more susceptible to corrosion take place. The corrosion current rate SS 304 and SS 316 alloys are 1.09 mA and 0.403 MPY, respectively. It can be concluded that addition Mo to Stainless Steel 316 improve corrosion rate due to Mo is stabilizer of passive film. Early study showed that corrosion SS 316 in chloride environment improved due to forming uniform passive layer [12].

![Tafel polarization curves obtained for Stainless steel SS 304 and 316 in nanofluid.](image1)

**Figure 3.** Tafel polarization curves obtained for Stainless steel SS 304 and 316 in nanofluid.

| Stainless steel | Corpot. mV | Anodic Tafel slopes βa (mV/dec) | Cathodic Tafel slopes βc (mV/dec) | Icor µA | CR mpy |
|-----------------|------------|-------------------------------|-----------------------------------|---------|-------|
| SS 304          | -148       | 0.769                         | 0.279                             | 1.09    | 0.503 |
| SS 316          | -176       | 0.327                         | 0.171                             | 0.403   | 0.186 |

### 3.4. X-ray diffraction

The stainless steel electrode of SS 304 and 316 were potentially polarized in nanofluid solution at 25 °C, after that time, the electrode was withdrawn and drying and finally examined by X-ray diffraction. Figure 4 a and b shows the diffractograms of SS 304 after polarization testing in nanofluid. XRD studies showed that the major phase for samples before polarization is associated with γ Fe phase as seen in Figure 4.a. After Tafel polarization testing, the peaks associated with γ Fe phase is still major phase in stainless steel. The scale of Fe2O3 associated with corrosion product of Fe cannot be seen in diffractograms. It can be concluded that corrosion stainless steel in adm + 0.01gpl nanoparticle ZrO2 is very low.

![XRD stainless steel 304 a) before b) after Tafel polarization in nanofluid.](image2)

**Figure 4.** XRD stainless steel 304 a) before b) after Tafel polarization in nanofluid.
3.5. Surface Morphology
Surface morphology of specimens stainless steel SS 304 and SS 316 after corrosion testing in nano fluid showed in Figure 5 a and b, respectively. In Figure 5a and 5b showed that the surface morphology specimen still smooth and free of corrosion product scale. From the data surface morphology stainless steel, it can be concluded that Nano fluid solution is not corrosive electrolyte.

![Figure 5. Surface morphology of stainless steel (5a) SS 304 and (5b) SS 316 after corrosion test in the Nano fluids.](image)

4. Conclusion
The corrosion behavior of the stainless steel SS 304 and 316 samples was studied in nanofluids contains 0.01 gpl nanoparticle alumina using the potentiodynamic polarization technique provided with XRD and SEM examinations. The results obtained can be summarized as follows:

The corrosion potential examination of the stainless steel SS 304 and SS 316 in nanofluid media contain 0.01gpl Al₂O₃ nanoparticle was actively corroded and the corrosion potential of SS 316 more negative compared with SS 304. The potentiodynamic polarization examination of the stainless steel SS 304 and SS 316 in nanofluid media contain 0.01gpl Al₂O₃ nanoparticle showed that the rate of corrosion of the stainless steel SS 304 and SS 316 in nanofluid was very low. The values of corrosion rate of these samples decreases in the order: SS 304 > SS 316. The increase in either Mo content in the stainless steels improves corrosion resistance.

5. References
[1] Djoko Hadi Prajitno 2015 Effects of scan rate on the corrosion behaviour SS 304 stainless steel in the nanofluid measured by Tafel polarization methods, AIP Conference Proceedings 1677, 070011
[2] Saidur R., Leong,K.Y.Leong, Mohammad,H.A., 2011. A review on applications and challenges of nanofluids, Renewable and Sustainable Energy Reviews, 15, 1646
[3] B.C. Pak, Y.I. Cho, 1998 Hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles, Exp. Heat Transfer 11, 151
[4] Ulzie Rea, Tom McKrell, Lin-wen Hu, Jacopo Buongiorno, 2009 International Journal of Heat and Mass Transfer 52, 2042
[5] Pop MGM, Brian GL 2008 Nuclear power plant using nanoparticles in emergency systems and related method, U.S. Patent: US 2008/0212733A1.
[6] Benoit Ter-Ovanesian*, Catherine Alemany-Dumont, Bernard Normand,, 2014 Electronic and transport properties of passive films grown ondifferent Ni-Cr binary alloys in relation to the pitting susceptibility Electrochimica Acta 133, 373
[7] Steven J.Zinkle, et., all. 2009. Structural Materials for fusion and fission energy, Material Today v.12 nov. 12
[8] Djoko Hadi Prajitno and dani G.S., 2017, Application Electrochemical Impedance Spectroscopy Methods to Evaluation Corrosion Behaviour of Stainless steels 304 in Nanofluids Media, Journal of Physics: Conf. Series 799, 012007
[9] Syarif D G and Prajitno D H 2013 Journal of Materials Science and Engineering B 3 2 122
[10] Gamry Potentiostat PCI4/G300, Electrochemical Measurement System 2010
[11] Gamry software DC 105 corrosion analysis system 2010
[12] J.M. Bastidas, C.L. Torres, E. Cano, J.L. Polo 2002 Corros. Sci. 44 625

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