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EFFECT OF SUBSTRATE SURFACE ROUGHNESS ON MORPHOLOGICAL AND TOPOGRAPHY OF NICKEL-ALUMINA THIN FILM

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ABSTRACT

Dip coating process promises good deposition of nickel-alumina catalyst on metal surface for various applications especially in gas conversion reaction. This study investigates the effect of different metal substrate roughness surface on nickel-alumina catalysts thin film formation. Three different stainless steel substrate roughness's used, 0.18 µm, 0.13µm, and 0.09µm. The solgel was prepare from Nickel (II) nitrate hexahydrate and Aluminum isopropoxide. After dip coating, the samples were being heat treated at 300°C for 90 minutes. These deposited thin film were characterized by using Atomic Force Microscopy (AFM). AFM result showed the presence of micro-sized, grain-like particles in the nickel-alumina topographical and morphological coating. Moreover, the AFM had clarify two main findings which are, thin film thickness and roughness is proportional to the substrate's roughness and also proportional to withdrawal speed. However, the withdrawal speed showed limitation of film formation due to drag gravitational force and coating speed factor. Charaterization of the deposited thin film samples had shown thickness of 0.5 – 6.0µm and roughness of 0.1 - 1.0µm.

Keywords: dip coating, substrate roughness, withdrawal speed, thin film, nickel-alumina.

INTRODUCTION

The nickel based metal is widely used as a catalyst for gas conversion reaction such as hydrogenation. The presence of catalyst will lead to faster reaction at certain operating temperature condition, by reducing the amount of energy required to initiate chemical reaction (Bej *et al*. 2013). This nickel based catalyst become suit for gas hydrogen industrial usage because of high selectivity potential, stable and also active through large inner surface to absorb large amount of reaction gas (Maluf *et al.* 2009).

The active nickel is typically metal which finely dispersed over support porous alumina or silica-based carrier. These value added resulting in large catalytically active surface area and huge quantities of hydrogen adsorption which act as the key characteristic of the reactions efficiency (Isha *et al.* 2012). Therefore, from the physical observation, nickel-alumina reaction integrated catalyst has a much larger volume per mass since the addition of support alumina, its also contributing of porous structures formation and increase the surface area of catalyst (Madon *et al,* 2015). Whereby, high surface area resulting of the nickel -alumina dispersion and create more active sites with small particle size from the porous structure (Silverwood *et al*. 2010).

Furthermore, nickel-alumina synthesized by sol gel through dip coating method has been reported to produce more stable support structure and higher nickel dispersion than conventional method such as impregnation (Zangouei *et al.* 2010). Basically the dip coating can be described as a process of dipping a substrate into a reservoir of sol-gel solution for some interval time until the substrate is completely wetted, and followed by withdrawing the substrate out from the sol-gel solution bath (Fang *et al*. 2008). These dipping process is crucial to the properties of coated thin film nickel-alumina catalyst on top of substrate's surface area (Mellor *et al*. 2001).

The purpose of this study is to observe the effect of substrate roughness on nickel-alumina thin film formation through dip coating method. By using constant nickel-alumina sol-gel concentration, correlate with various substrate roughness and different withdrawal speed of dip coating were applied in this experiments. Moreover, by comparing the results obtained with the dip coating models in the literature, it is expected to yield the critical information regarding substrate's roughness effects for further optimization from a practical viewpoint.

MATERIALS AND METHODS

Materials

In this experiment, stainless steels grade 304 were used as substrates with a specific dimension of 20mm width x 100mm length x 1.2mm thickness.

Sol-gel solutions were prepared using Nickel(II) nitrate hexahydrate - $Ni(NO_3)_2{\cdot}6H_2O$ and Nitric Acid 65% - HNO_3 obtained from R and M Chemicals, Aluminum isopropoxide - $Al[OCH(CH_3)_2]_3$ from Acros Organics, and Ethanol 99.8% obtained from Chem AR System.

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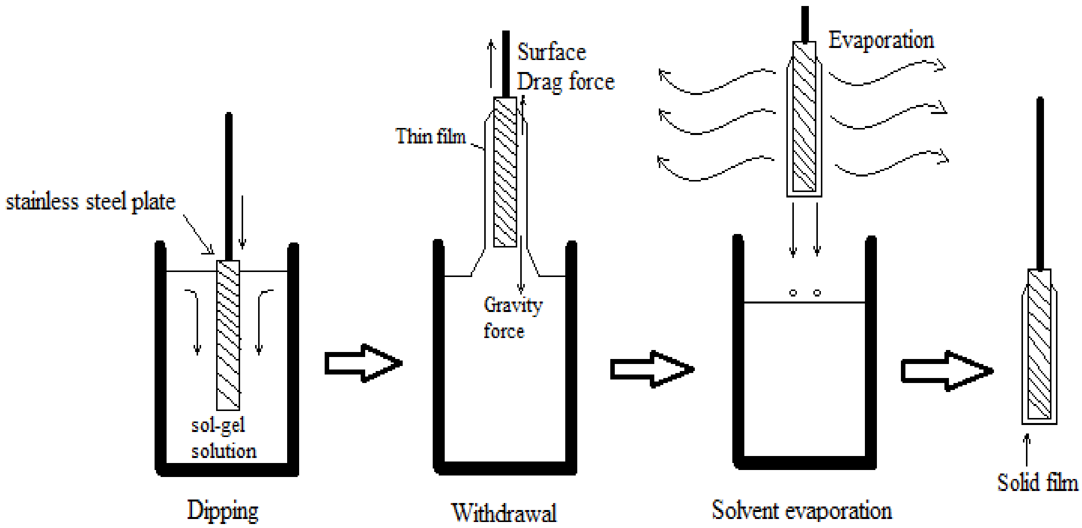

Figure-1. Schematics diagram of dip coating process.

Substrate preparation

The substrates were cleaned using Skymen JP-020S ultrasonic cleaner to remove dust and oily contamination on the substrate surface. Cleaned stainless steel were polished using abrasive paper each. In order to get different types of roughness, three grade of abrasive paper were used, which are 400, 800 and 1200. Each substrates were polished in one way direction for 30 cycles.

Prior to dipcoating, substrates surface roughness was examined using Mitutoyo SJ-400 surface roughness tester. The purpose of this testing was to determine the roughness value of the substrate surface. The equipment involved was.

Sol-gel preparation

For the preparation of sol gel, firstly 22g Aluminum isopropoxide were dissolved with mixture solution of 90ml ethanol, 5ml Nitric acid and 5ml distill water. Than the solution was stirred at 60° C until homogenous for one hour. Then, 10g of Nickel(II) nitrate hexahydrate was added slow and continuously into the solution and kept stirred at 60° C until homogenous for one hour. After completing the mixing process, sol-gel were stored in Scott bottles for degassing and aging process. It was kept in the dry box and maintain at room temperature and humidity less than 40%.

Dip coating process

The dip coating schematic diagram is shown as Figure-1. The equipment used for dip coating process was PTL-MM01 Dip Coater with dipping and withdrawal speed range of 1-200 mm/min. For dip coating sector, the dipping and withdrawal speed used were 40, 80, 120, 160, and 200 mm/min. The 304 stainless steel plate were immersed into the solution and an uncoated area was kept on the top of the plate. The plate was then withdrawn from the bath at a prescribed withdrawal velocity. The coated sample is pursued evaporation process for 20 minutes. Then, followed by heat treatment of isothermal annealing by using Carbolite RHF 14/3 box furnace at operating temperature of 300 °C for 90 minutes.

Thin film characterization

The thin film catalyst were characterized using Atomic Force Microscopy, AFM (XE-100 Park Systems) which provided a 3D profile of the surface in nano scale.

RESULTS AND DISCUSSIONS

Substrate surface roughness

The substrates were tested with surface roughness tester to determine the result of the polishing using three different abrasive paper grades. The tests were conducted at four different points to get the average surface roughness. As shown in Table-1, the highest surface roughness 0.18 µm is from abrasive paper grade 400, meanwhile the lowest 0.09 µm is from the abrasive paper grade 1200.

Surface topography and morphological

The AFM images as in Figure-2, clarify that the nickel-alumina thin film coating for surface roughness is proportional to the substrate roughness. Given that sample surface roughness is 0.906µm, 0.622µm and 0.428µm for substrate 0.18µm, 0.13µm and 0.09µm. The morphology shown by the peaks and valleys patterns which exhibited in the form of contours, provide quantitative indication of the surface roughness and absorptancy of the coatings by Ra values, similar reported by Amri *et al*. 2012. Meanwhile for topology had shown as same by Ramzan *et al*. 2015, whereby the presence of micro-sized, grain-like particles in the nickel-alumina.

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Table-1. Substrate surface roughness.

No	Abrasive paper grade	Surface roughness Ra (μm)
1	400	0.18
2	800	0.13
3	1200	0.09

Thin film thickness

The experimental results of the thin film thickness versus the withdrawal velocity of dip coating process for each substrate roughness are shown in Figure-3. In Section I, thin film thickness (h) tendency is proportional to the withdrawal velocity, due to the viscous pull drag factor of steel plate surface on sol-gel solution. At a higher velocity, a greater amount of the liquid is pulled which results in a thicker film. Figure-3 also shows that the higher substrate roughness leads to the increase of thin film thickness, (h) formation rate which is also similar to work done by Fang *et al*. 2008. The substrate roughness of 0.18μm, 0.13μm and 0.09μm yield of standard deviation 0.48, 0.67 followed by 0.93. Its clearly shown that 0.09μm substrate become most consistent roughness Meanwhile for Section II, slightly indicates the decrease of thin film thickness with increase of the withdrawal velocity. This is the point of maximum nickel-alumina thin film thickness formation.

The value of maximum velocity differs with each substrate roughness and quite low for smoother substrate. Based on Fang *et al.* 2008 and Isha *et al*. 2012, this work is defined that in Section I, the thickness of the coating film increases as the viscous pull drag is proportional to withdrawal velocity. However as υ further increases in Section II, higher amount of sol gel solution was pulled up in a relatively shorter time. With the lack of sufficient evaporation time, the gravity force leads the sol gel solution drown back into pool before the solid sol-gel thin film manage to be formed completely on the substrate surface. The outcome of the withdrawal speed factor had created a competition between drag force (solution film moving upward) and gravity (solution film moving downward) as shown in Figure-1 which determines the variation of final solid nickel-alumina thin film thickness which is similar to the reported by Zangouei *et al*. 2010.

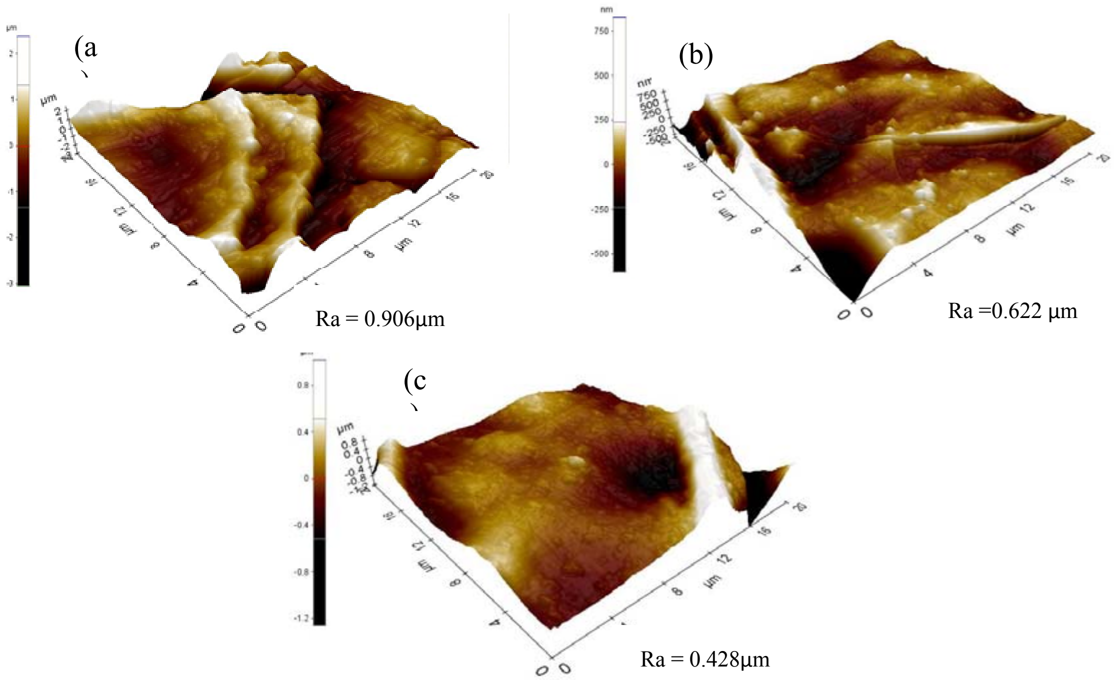

Figure-2. AFM image of the nickel-alumina for a) Substrate surface roughness 0.18 μm; b) Substrate surface roughness 0.13 μm; c) Substrate surface roughness 0.09 μm.

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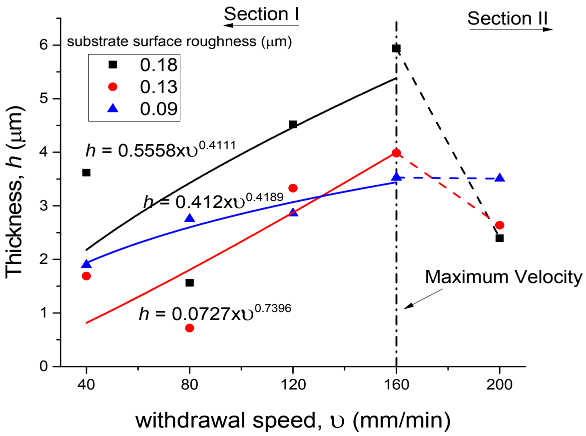

Figure-3. Thin film thickness versus the withdrawal speed of dip coating process for each substrate roughness.

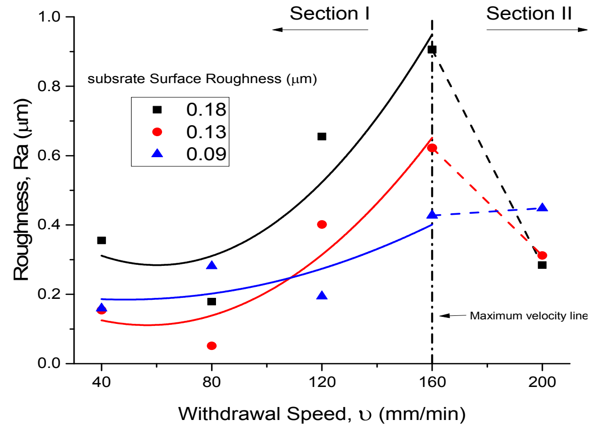

Figure-4. Thin film surface roughness against withdrawal speed for different substrate roughness.

Models fitting

According to (Fang *et al*., 2008), earliest analysis of the dip coating process was a one-dimension infinite long plate drawn out of a wetting bath. The analysis was based on the hydrodynamics equations of Newtonian fluid. The relationship between the film thickness and withdrawal speed is given as,

$$h \alpha \upsilon^{x} \qquad (1)$$

where h is the thickness of the coated layer and υ is the withdrawal speed. A wide range of values x found experimentally have been reported. The curves in Section I of Figure-3 are fitted based from Equation (1).

Thin film surface roughness

The experimental result of coated film roughness against withdrawal speed of dip coating process is shown in Figure-4. In Section I, the tendency shows that surface roughness is proportional to the withdrawal speed, meanwhile in Section II, the plots indicate the decrease in film surface roughness. This break point clearly shows that surface roughness has maximum value at certain withdrawal speed condition similar to the reported by Fang *et al*. 2008. The substrate roughness of 0.18μm, 0.13μm and 0.09μm yield of standard deviation 0.73, 0.78 followed by 0.96. It's clearly shown that 0.09μm substrate become most consistent roughness.

The Figure-4 shows that the higher substrate roughness leads to the increase of thin film surface roughness formation rate and this result almost similar to the work of Ramzan *et al*. 2015.

Based on report by Fang *et al*. 2008 and Silverwwod *et al*. 2010, the drag force and gravity factor that occurred during withdrawal speed process has leads to the break maximum point surface roughness formation.

CONCLUSIONS

Nickel-alumina catalysts have been successfully coated on stainless steel substrates with surface roughness of 0.09μm, 0.13μm, and 0.18μm. The result obtained from AFM had clarify two main findings which are, thin film thickness and roughness are proportional to the substrate's roughness and also proportional to the withdrawal speed of dip coating. But for the withdrawal speed had shown limitation of film formation was observed due to drag gravitational force and coating speed factor.

Charaterization of substrate roughness effect on deposited thin film morphology and topology had shown uneven of thickness and roughness formation. These result obey the hydrodynamics equations of Newtonian fluid (Fang *et al*. 2008), but at comparative 3 different substrate roughness parameter, it has shown unevent thickness and roughness distribution due the range used is to small and difficult to show clear different of *h* value. Therefore, we can conclude that the substrate roughness parameter is not the main influence factor to the nickel-alumina thin film formation. Furthermore, this study had come out with surface roughness of 0.09μm yield the highest (near to 1) of standard deviation value for all tested parameter compared to the others, and became the most suitable candidates for coating substrate due its consistency. For future studies, it's suggested to pursue on correlation of variable sol gel concentration and calcination temperature to withdrawal speed at substrate surface roughness of 0.09 μm should be made, in order to investigate other major influence factors of nickel-alumina thin film formation characteristics.

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