Diffusion and Bonding Mechanism of Protective γ-Al_2O_3 on FeCrAl Foil for Metallic Three-Way Catalytic Converter

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Abstract. High pollutant level contributed by mobile sources/land transportation that become main problems for the human health. Improving exhaust emission system by improving catalytic converter properties is one of the most effective way to produce healthy air in our environment. It is conducted by two methods i.e. ultrasonic during electroplating (UBDEL) and electroplating process (EL) which are not fully investigated yet as catalytic converter coating process. UBDEL is conducted using sulphamate types electrolyte solution, Frequency of 35 kHz, current of 1.28A, Voltage of 12 V, and various time of 15, 30, 45, 60 and 75 minutes. Meanwhile El method is conducted using parameters of current of 1.28A, Voltage of 12 V, stirrer speed of 60 rpm and various time of 15, 30, 45, 60 and 75 minutes. Fully γ-Al_2O_3 bonding to the FeCrAl substrate is shown by UBDEL 75 minutes samples proved by SEM images and Ra and Rq are 4.01 μm and 5.64 μm, respectively. Ni present on the FeCrAl substrate as other protective layer generated by Ni electroplating process that will improve thermal stability of FeCrAl at high temperature of 1000 ^{0}C. From the results, can summarized that UBDEL technique is promoted as an effective catalytic converter coating technique.

1 Introduction

The first strict regulation to control automobile emissions was introduced through a US Clean Air Act, 1970, in the United States of America. In addition, Mobile sources contribute for about 44% of outdoor toxic emissions, approximately 50% of cancer risk and at around 74% of non-cancer risk health problems. The technology for removing pollutants in the exhaust system is catalytic converter that first developed in 1965 [1, 2]. The location of the catalytic converter in the car is shown in Figure 1.

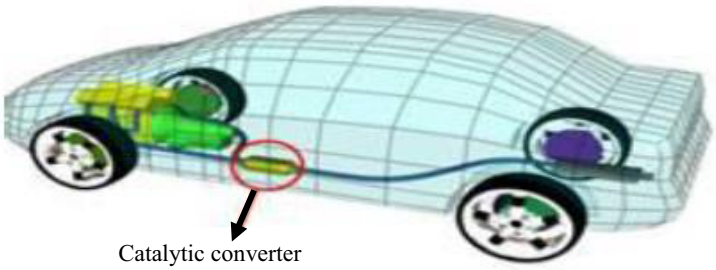

Figure 1. Location of catalytic converter in passenger car [3]

Nowadays, the metallic catalytic converter of FeCrAl was interesting component to explore due to their advantages in the high-temperature corrosion resistance, including strong adherence of oxide film on the surface of substrate [4, 5]. FeCrAl is consists of 5-8 wt% aluminium, 17-22 wt% chromium and reactive element to improve oxide adhesion and oxidation resistance [6]. Command washcoat material such as Al_2O_3, SiO_2, TiO_2, or SiO_2- Al_2O_3 [7]. However, γ-Al_2O_3 washcoat material not fully explored even though it promising several advantages such as low price, high surface area, good chemical stability, high micro-hardness, and wear resistance at high-temperature [8]. Therefore, in this research the FeCrAl is coated by γ-Al_2O_3 powder which can result higher surface area of about 100 m^2/g.

There are several method for coating FeCrAl substrate such as dip coatings, which combined with some pre-treatments, such as growing a number of textured alumina whiskers on the surface of the metal support and shortened the diffusion path before depositing the washcoat [9, 10]. The other methods are co-precipitation, sol-gel and spray-pyrolysis methods [11], electrophoretic deposition [12], solution combustion synthesis (SCS) [13], aluminizing technique [14], and hydrothermal method [15, 16]. That method presented good adherence to the substrate, decreasing surface roughness and closed

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the surface porosity of the substrate [17]. However, the existing methods still have some limitations, especially due to the rather complicated method to applying the catalyst which is in the form of powder.

Material coated by Al_2O_3 promote high surface roughness which important to the filtration and catalyst application [17]. Roughness of the material indicates the surface topography which have several forms such as digs, pits, dust particle, scratches, machining marks on machine surface, polishing marks on optical surface, granularity, crystallite in film deposited in surface and electro-polishing [18]. According to Putrasari et al., (2010) [19] that surface roughness of FeCrAl coated by SiC and Al_2O_3 is successfully developed using ultrasonic technique for 10 min in frequency of 35 kHz and it improve high thermal stability of FeCrAl substrate and homogeneity of Ni electroplating layer. However, it still need improvement and special treatments. In other hand, diffusion of aluminium alloy (FeCrAl) is very challenging to investigate since some phenomena occurred. Less protective γ-Al_2O_3 powder is caused by slow diffusion of Al alloy to the metal oxide interface to compensate for the aluminum consumption. Oxidation behavior of the aluminium alloy is measure by diffusion coefficient [20]. The growth mechanism occurred by both cation and anion transport in the Al_2O_3 scales on Fe-Cr-Al. The alumina scale grows exclusively by oxygen diffusion along grain boundaries. Diffusion results were also obtained in alumina developed on γ-NiAl by cationic and anionic self diffusion tests and also by an electrochemical method [21].

Therefore, the diffusion phenomena of the coated FeCrAl and its surface roughness treated by electroplating approach is very challenging to investigated. It believe that electroplating approach to promote fully embedded of γ-Al_2O_3 powder to FeCrAl substrate that figured by SEM/EDS and surface roughness testing.

2 Methodology

FeCrAl foils was treated using various novel Nickel electroplating technique i.e. electroplating ultrasonic bath during electroplating technique. It coated by γ-Al_2O_3 powder with crystallite size of 121.68 μm which measured by X-Ray Diffraction (XRD) machine. In this research, electrolyte used in electroplating process is called by sulphamate types which consist of nickel (II) sulphamate 6-hydrate ($NiSO_4.6H_2O$), nickel (ii) chloride ($NiC_{l2}·6H_2O$), boric acid (H_3BO_3), and sodium dodecyl sulfate ($C_{12}H_{25}OSO_3.Na$) which believed that it can optimize the electroplating process.

2.1 Nickel (Ni) electroplating process (EL sample)

Nickel electroplating was carried out using some equipments and components such as DC power supply, anode (Ni plate), cathode (FeCrAl foil), electrolyte solution, magnetic stirrer and hot plate for adjust temperature and stir speed as well as electronic microbalance. Ni plate and FeCrAl foil is cropped at the fix size of 50 mm x 10 mm and 40 mm x 20 mm respectively. Preparation of electrolyte solution with the composition is shown in Table 1.

Table 1. Composition of electrolyte solution

Electrolyte solution	Weight (gr)	Composition (%)
$NiSO_4.6H_2O$	10.2	51.28
$NiC_{l2}·6H_2O$	0.2	0.85
H_3BO_3	1.2	5.12
$C_{12}H_{25}OSO_3.Na$	8.4	42.73

Electrolyte solution is prepared with distilled water at constant temperature of 60 ^{0}C, distilled water volume of 0.25 L, holding time approximately of 10 minutes and pH value is adjusted of 2.5-5. Electroplating process was conducted using various times of 15, 30, 45, 60 and 75 minutes, current of 1.28 A, voltage of 12 V, distance between anode and cathode of 25 mm, mass of γ-Al_2O_3 powder of 5 g and total surface area of 1600 mm^2 in two sides. The schematic diagram of electroplating process is shown in Figure 2.

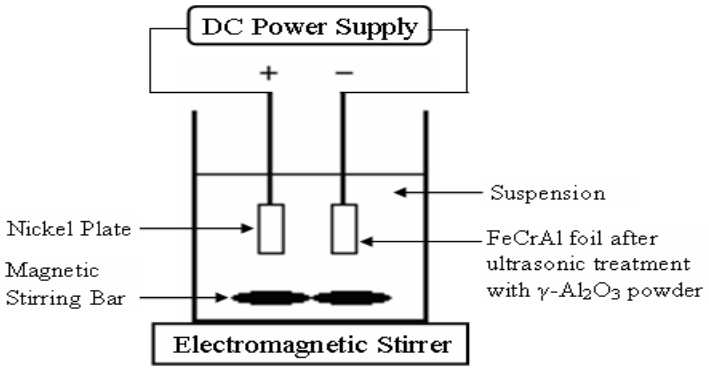


Figure 2. Schematic diagram of electroplating process

2.2 Ultrasonic bath during electroplating technique (UBDEL)

Basic principle of UBDEL is similar with electroplating technique. However, in this technique have a unique methods where transducer as frequency sources is generated in electroplating technique as replacement of magnetic stirrer. Electrolyte solution is prepared with distilled water at constant temperature of 60 ^{0}C, distilled water volume of 0.25 L, holding time approximately of 10 minutes and pH value is adjusted of 2.5-5. UBDEL technique was carried out using various times of 15, 30, 45, 60 and 75 minutes, frequency of 35 kHz, current of 1.28 A, voltage of 12 V, distance between anode and cathode of 25 mm, mass of γ- Al_2O_3 powder of 5 gr. The schematic diagram of UBDEL technique is shown in Figure 3. The specification of ultrasonic machine is listed in Table 2.

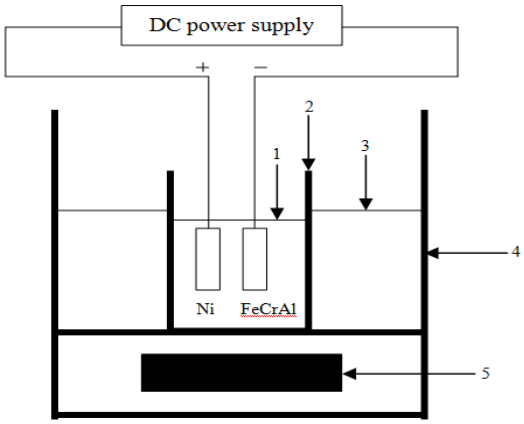


Figure 3. Schematic diagram of ultrasonic bath during electroplating where (1) Electrolyte solution; (2) Beaker; (3) Water; (4) ultrasonic tank; (5) Ultrasonic source

Table 2. Technical specification of ultrasonic bath machine

Description	Nominal
Bath dimension	Ø 24.5 cm and 13 cm deep
Effective capacity	5.6 litters
Insert tray	Ø 22.5, 11.5 cm deep with mesh 10 x 10 mm
Sound level	2 x 240 Watt/ period or 35 kHz
Power input	140 Watt
Weight	Net 5.5 kg, and gross 8 kg
Dimension w x d x h	27 x 27 x 27 cm

All the samples are characterized using Scanning Electron Microscopy (SEM) which is coupled by Energy-Dispersive Spectroscopy (EDS) and surface roughness machine. SEM is generated using magnification of 300 times while Surface roughness machine is arranged by λ_c of 0.8 mm, λ_s of 2.5 µm, eva-L of 4 mm and Roughness range of 800. Surface roughness and surface roughness mean squared could be measured manually using the Eq. 1 and Eq 2 respectively [22].

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|y_i| \quad (1)$$

$$R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n}y_i^2} \quad (2)$$

Where;
Ra is surface roughness, Rq is surface roughness mean squared, n is equally spaced points along the trace, yi is is the vertical distance from the mean line to the i^{th} data point.

3 RESULT AND DISCUSSION

3.1 Influence of electroplating approach to the coating surface and composition

Figure 4 to 14 show the surface morphology of coated and uncoated FeCrAl by γ-Al_2O_3 powder using ultrasonic during electroplating and electroplating technique. Figure 4 shows the uncoated sample with even surface that consist of C, O, Al, Cr and Fe. Figure 5 to Figure 9 show the samples that treated by ultrasonic during electroplating with the various times of 15, 30, 45, 60 and 75 minutes, respectively. There are many unrelated chemical is detected in those samples such as Sodium (Na) for 6-12 %mass and Sulfur (S) for 0-6%mass because the electrolyte used in this process is contain Na and S. Therefore, there is bonding activity between those chemical and coated FeCrAl. Nickel (Ni) present 11-32 % mass in the coated samples because Ni plate is performed during this process. From the UBDEL samples can be seen that the bonding activity for surface γ-Al_2O_3 powder and electrolyte chemical is successfully achieved. Fully embedded of γ-Al_2O_3 in line with the time increment. It approved by surface roughness analysis that the UBDEL 75 minute samples has highest surface roughness for 4.01 µm as compared to other UBDEL samples. The full bonding phenomena of UBDEL samples proof that the jet flush energy or high speed bubbles promote to the γ-Al_2O_3 powder to bond on the FeCrAl substrate [19]. Fully bonding activity is related to the high diffusion of γ-Al_2O_3 to the FeCrAl substrate since there is cation and anion transport which promote higher diffusion coefficient [20].

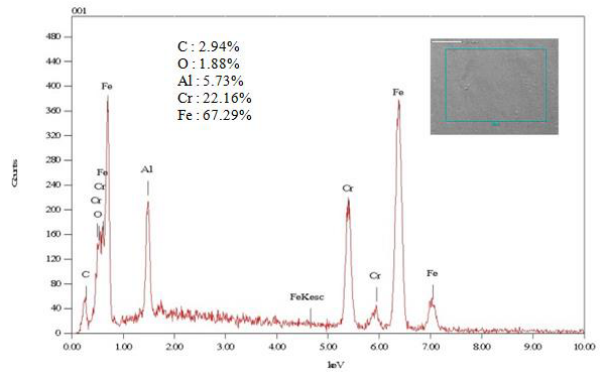


Figure 4. SEM & EDS image for Raw material

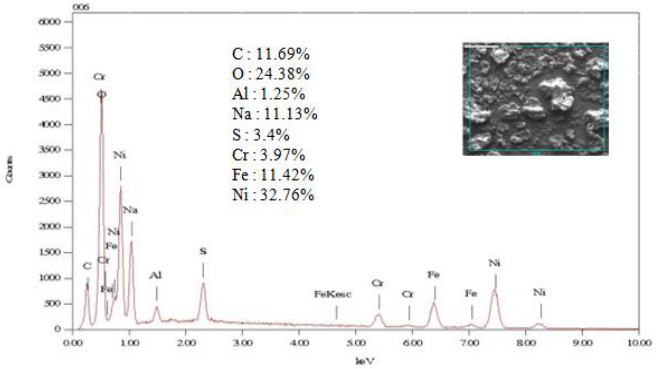


Figure 5. SEM & EDS for UBDEL 15 min

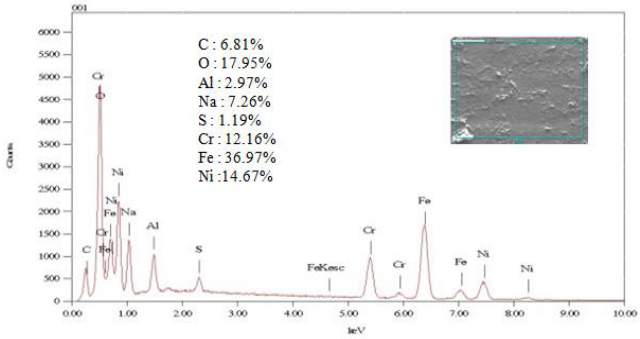


Figure 6. SEM & EDS for UBDEL 30 min

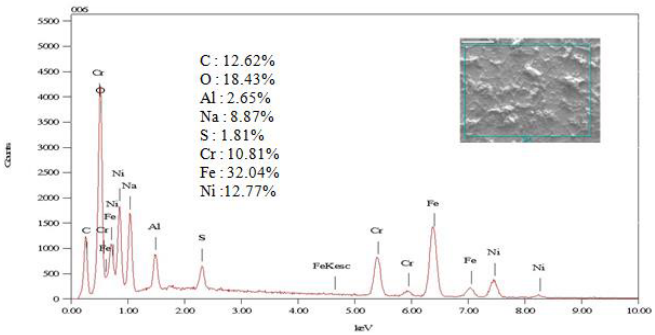


Figure 7. SEM & EDS for UBDEL 45 min

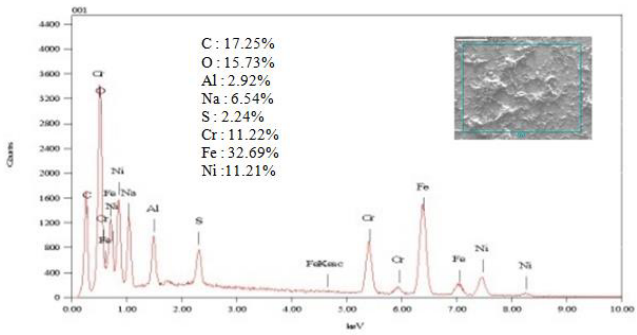


Figure 8. SEM & EDS for UBDEL 60 min

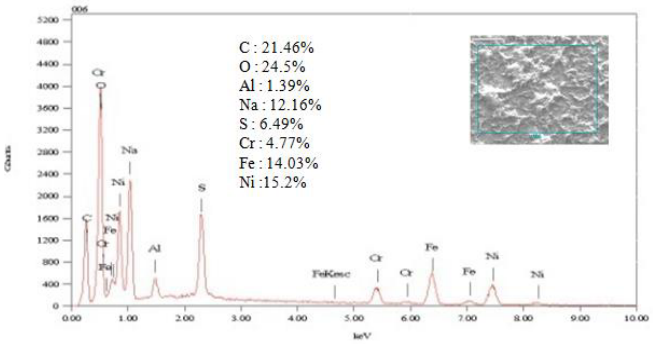


Figure 9. SEM & EDS for UBDEL 75 min

Figure 10 to Figure 14 shows the EL samples with the various electroplating times of 15, 30, 45, 60 and 75 minutes, respectively. The influence of electrolyte to electroplating process is shown in EDS analysis that the Na (2-13 %mass) and S (0-4 %mass) chemical present on coated FeCrAl surface. It will play the important role when the coated material is performed in high temperature of 1000 ^{0}C. The γ-Al_2O_3 as main coated material is increased with time performed increased as well. It approved by surface roughness of 1.06 µm as the highest number as compared to other EL samples.

Besides that Ni has observed in the EDS analysis of coated FeCrAl for 6-25 %mass. It is promote the protection at high temperature [23] because appear intensive co-precipitated NiO-Al_2O_3 system [24]. Interaction between γ-Al_2O_3 and FeCrAl substrate is related to the diffusion activity where the alumina scale grows exclusively by oxygen diffusion along grain boundaries. Higher Al content and Oxygen content will promote higher diffusion phenomena of the samples [20].

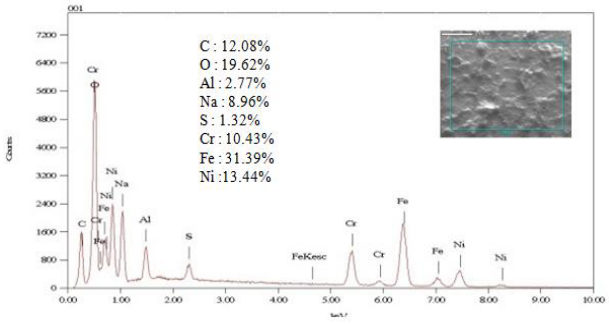


Figure 10. SEM & EDS for EL 15 min

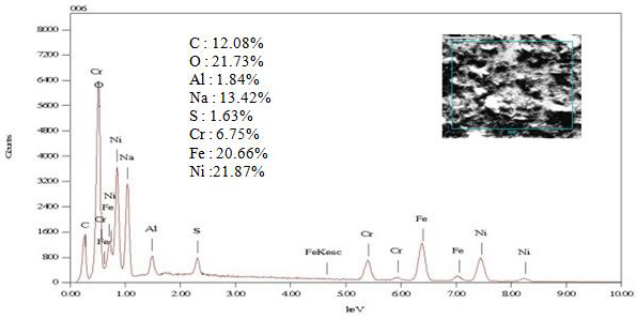


Figure 11. SEM & EDS for EL 30 min

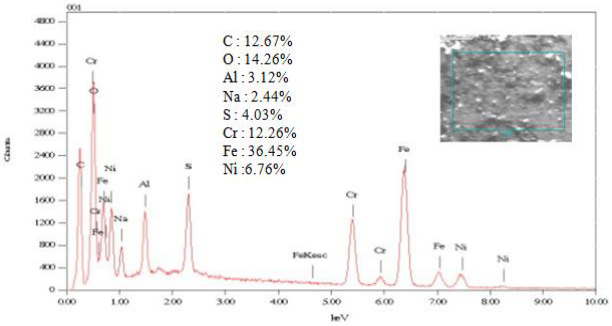


Figure 12. SEM & EDS for EL 45 min

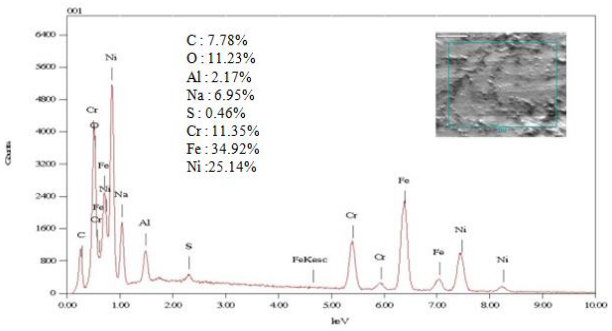


Figure 13. SEM & EDS for EL 60 min

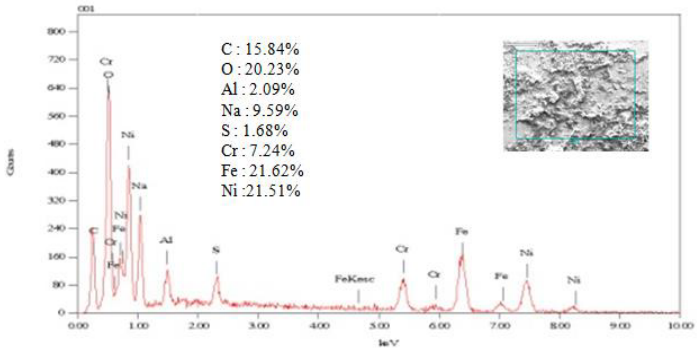
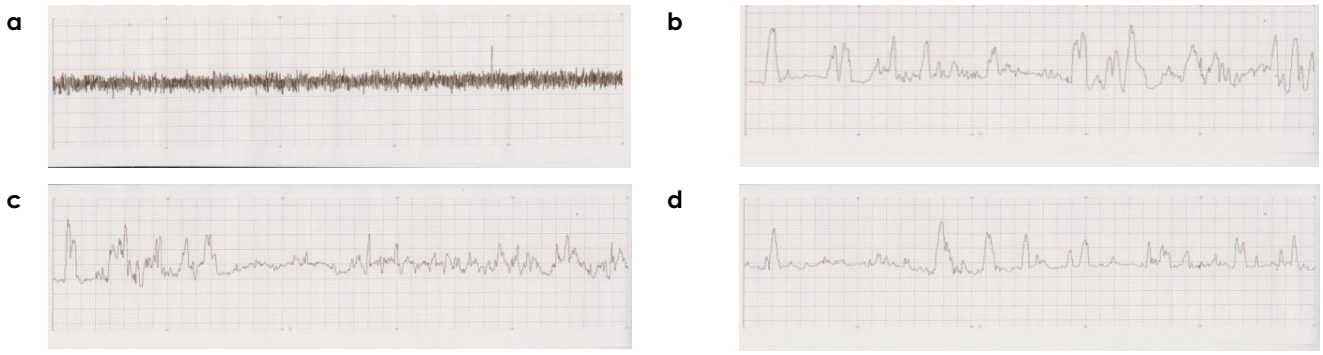


Figure 14. SEM & EDS for EL 75 min

3.2 Surface roughness (Ra) and surface roughness mean squared (Rq) analysis

Figure 15 shows the surface roughness (Ra) of coated and uncoated samples which called by raw material, UBDEL samples and EL samples. Those samples have different Ra influenced by different treatment times of 15, 30, 45, 60 and 75 minutes. surface roughness for sample raw material is 0.02 µm, for the UBDEL samples shown by Figure 15 b to f i.e. 3.35 µm, 1.22 µm, 2.04 µm, 1.59 µm and 4.01 µm, respectively. Surface roughness of El samples shown in Figure 15 g to k i.e. 1.04 µm, 0.7 µm, 0.92 µm, 1.05 µm and 1.06 µm respectively. The fluctuate Ra value by different treatment times is caused by many several factors such as electrolyte chemical bonding, unstable atmospheric environment and diffusion activity of γ-Al_2O_3 into FeCrAl during treatment.



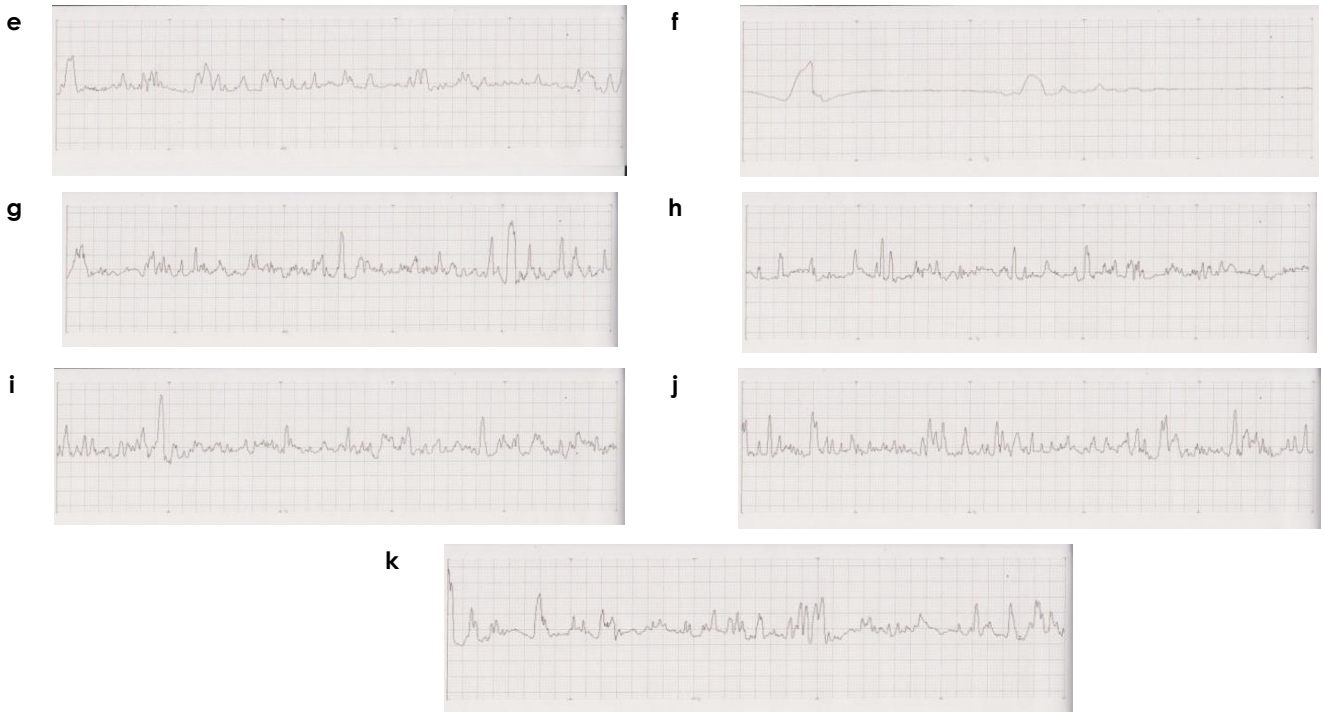


Figure 15. Surface roughness of a: Raw material, b:UBDEL 15 min, c: UBDEL 30 min, d: UBDEL 45 min, e: UBDEL 60 min, f: UBDEL 75 min, g: EL 15 min, h: EL 30 min, i: EL 45 min, j: EL 60 min and k: EL 75 min

The other parameter such as surface roughness mean squared (Rq) also presented by Figure 15 a to k i.e. 0.03 µm, 4.38 µm, 1.57µm, 2.87 µm, 2.05 µm, 5.64 µm, 1.46 µm, 0.94 µm, 1.25 µm, 1.42 µm and 1.46 µm, respectively. Lowest Ra and Rq are shown by raw material for 0.02 µm and 0.03 µm since there is no coating activity for the FeCrAl substrate. The highest Ra and Rq are shown by UBDEL 75 minutes for 4.01 µm and 5.64 µm. It shown the higher number as compared to other UBDEL samples and EL samples. It may caused by the combination between electrical activity sourced by DC power supply and ultrasonic frequency which led to effective coating activity. High speed bubbles combined by cathode-anode interaction may promote better bonding and diffusion process of γ-Al_2O_3 and FeCrAl substrate.

4 Conclusion

Coating process of FeCrAl substrate by γ-Al_2O_3 powder is successfully conducted using ultrasonic during electroplating and electroplating process. There are several phenomena tha has been observed such as:

1. Fully bonding of γ-Al_2O_3 into FeCrAl is shown by UBDEL 75 minutes sample where increasing holding time will increase bonding activity of washcoat material to the substrate material.
2. Surface roughness of the samples is defined by how many particle of powder and chemical agent which ebbed into the substrate. surface roughness of the EL samples is lower than UBDEL samples where highest Ra and Rq are 4.01 µm and 5.64 µm.
3. There are several chemical observed by EDS analysis such as O, C, Ni and Na which promote developing NiO- γ-Al_2O_3, C- γ-Al_2O_3 and NaO-γ-Al_2O_3 form. That form believe that it can be increased thermal stability of developed substrate.

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References

1. R.M. Heck, and R. J. Farrauto, Automobile Exhaust Catalyst. Applied Catalysis. A: General, **221**, 443-457 (2001).
2. S. Darwin, U. Puji, R. Hamimah Abd. and H. Shahrin. Conceptual Design of Catalytic Converter. International Advanced Technology Congress 2005, Kuala lumpur, Malaysia (2005).
3. J.M. Pardiwala, F. Patel and S. Patel. Review paper on Catalytic Converter for Automotive Exhaust Emission. International Conference On Current Trends In Technology, NUiCONE, 382-481 (2011).
4. D. Pilone. Ferritic Stainless Steels for High Temperature Applications in Oxidizing Environments. Recent Patents on Materials Science, **2**, 1, 27-31, ISSN 1874-4648, (2009).
5. T. Amano, Y. Takezawa, A. Shiino and T. Shishido. Surface Morphology of Scale on FeCrAl (Pd, Pt, Y) alloys. Journal of Alloys and Compounds, **452**, 1, 16-22 (2008)

6. J.R. Nicholls and W.J. Quadakkers. Materials Issues Relevant to the Development of Future Metal Foil Automotive Cataltic Converters. In: Materials Aspects in Automotive Catalytic Converters, Hans Bode (Ed.), 31-48 (2002).
7. R.M. Heck, R.J. Farrauto and S.T. Gulati. Catalytic Air Pollution Control Commercial Technology, 3rd ed, John Wiley & Sons, New Jersey, ISBN 978 -0-470-27503-0 (2002).
8. N.A. Badarulzaman, S. Purwadaria, A.A. Mohamad, & Z.A. Ahmad. The Production of Nickel–Alumina Composite Coating via Electroplating. Ionics, **15**, pp. 603-607 (2009).
9. S. Zhao, J. Zhang, D. Weng, and X. Wu. A Method to Form Well-Adhered γ- Al_2O_3Layers on FeCrAl Metallic Supports. Surface and Coating Technology, **167**, 1, 97-105 (2003).
10. L. Jia, M. Shen and J. Wang. Preparation and Characterization of Dip-Coated γ-Alumina Based Ceramic Materials on FeCrAl foils. Surface & Coatings Technology, **201**, 16-17, 7159–7165 (2007).
11. Z. Yanqing, X. Jieming, L. Cuiqing, X. Xin and L. Guohua. Influence of Preparation Method on Performance of a Metal Supported Perovskite Catalyst for Combustion of Methane. Journal of Rare Earths, **28**, 1, 54-58 (2010).
12. I. Corni, M.P. Ryan, and A.R. Boccaccini. Electrophoretic deposition: From Traditional Ceramics to Nanotechnology. Journal of the European Ceramic Society, **28,** 7, 1353–1367 (2008).
13. A. Specchia, A. Civera, and G. Saracco. In-Situ Combustion Synthesis of Perovskite Catalysts for Efficient and Clean Methane Premixed Metal Burner. Chemical Engineering Science, **59,** 22-23, 5091-5098 (2004).
14. X. Wu, D. Weng, S. Zhao and W. Chen. Influence of An Aluminized Intermediate Layer on The Adhesion of a Gamma-AL2O3 Washcoaton FeCrAl. Surface & Coatings Technology, **190,** 2-3, 434– 439 (2005).
15. J.M. Zamaro, M.A. Ulla, and E.E. Miro. ZSM5 Growth on a FeCrAl Steel Support. Coating Characteristics Upon the Catalytic Behavior in The NOx SCR. Microporous and Mesoporous Materials, **115**, 1-2, 113–122 (2008).
16. M.V. Sivaiah, S. Petit, M.F. Beaufort, D. Eyidi, J. Barrault, C. Batiot-Dupeyrat and S. Valange. Nickel Based Catalysts Derived from Hydrothermally Synthesized 1:1 and 2:1 Phyllosilicate as Precursors for Carbon Dioxide Reforming of Methane. Microporous and Mesoporous Materials, **140**, 1-3, 69-80 (2010).
17. T.Y. Liu, Lay-Gaik, Teoh, Chao-Kai Huang, Ying-Chieh Lee. A Study of Roughness Improvement of Al2O3 Substrates Using Sol-Gel method. Procedia Engineering **141**, 108–114 (2016).
18. L. Henke. An AFM determination of the effects on surface roughness caused by cleaning of fused silica and glass substrates in the process. Biosensors and Bioelectronics, **17**, 547-555 (2002).
19. Y. Putrasari, P. Untoro, S. Hasan, Huda, and D. Sebayang. Modification of Surface Roughness and Area of FeCrAl Substrate for Catalytic Converter using Ultrasonic Treatment. Journal of Mechatronics, Electrical Power, and Vehicular Technology, **01**, 2 (2010).
20. A. Heesemann, E. Schmidtke, F. Faupel, A. Kolb-Telieps, and J. Klower. Aluminum And Silicon Diffusion In Fe-Cr-Al Alloys. Scripta Materialia, **40**, 5, 517–522 (1999).
21. K. Messaoudi, A.M. Huntz and B. Lesage. Diffusion and growth mechanism of Al_2O_3 Fe-Cr-Al alloys scales on ferritic. Materials Science and Engineering, **A247**, 248–262 (1998).
22. E.P. Degarmo, J. Black and R.A. Kohser. Materials and Processes in Manufacturing **223**, ISBN: 0-471-65653-4 (2003).
23. L. Xiang, Y.L. Gong, Li, and Z.W. Wang. Influence of Hydrothermal Modification on the Properties of Ni/ Al_2O_3 Catalyst. Applied Surface Science, **239**, 94–100 (2004).
24. E. Kis, R. Marinkovic-Neducin, G. Lomic, G. Boskovic, D.Z. Obadovic, J. Kiurski, and P. Putanov. Structural and textural properties of the NiO- Al_2O_3 catalyst. Journal of Polvhedron, **17**, 1, 27-34 (1998).