Effect of Material Composition on Thermal Stability Analysis of Coated and Uncoated FeCrAl CATCO by γ-Al₂O₃ Ultrasonic-Electroplating Technique

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Abstract: Catalytic Converter (CATCO) material become an interesting field to investigate due to the common CATCO material being ceramic material that has high brittleness than metallic materials. Therefore, this research investigates the FeCrAl metallic material as CATCO substrate that is coated by γ-Al₂O₃ as a washcoat, Nickel Oxide (NiO) as a catalyst. The coating analysis was performed by ultrasonic using a frequency of 35 kHz and various ultrasonic times of 1, 1.5, 2, 2.5, and 3 hours and electroplating technique by sulphamate types electrolyte using variation times of 15, 30, 45, 60, and 75 minutes, a current density of 8 A/dm². The result shows that the raw material was consists of Fe, Cr and Al with Fe element was dominated for 74.13wt%. Coated sample by ultrasonic consists of Fe, Cr, Al, O, and C elements due to FeCrAl substrate was deposited by γ-Al₂O₃ powder and by electroplating technique consists of Fe, Cr, Al, O, C, Ni and Na elements due to NiO deposition as catalyst material. TGA analysis observed that the highest mass change was observed by raw material 23.39 mg and UB+EL 30 min samples for lowest mass change of 2.85 mg with a point of the reaction is 0.07 mg/min may be caused by a protective oxide layer that developed during the coating process. Therefore, the coated metallic CATCO has a promising prospect to replace the ceramic CATCO due to high thermal stability by protecting layer and low mass change.

Keywords: Catalytic converter, metallic material, thermal stability, ultrasonic, electroplating

1. Introduction

The metallic CATCO was interesting component to explore as compared to ceramic materials due to its cheaper, high ductility and high thermal stability up to 1500 °C. The FeCrAl is generally considered as metallic substrates in this research due to their advantage in the high thermal stability, high corrosion resistance, including the strong adherence of oxide film on the surface of substrate when applied the appropriate surface treatment [1,2]. The existing of excellent oxidation catalyst materials was usually based on the precious metal (Platinum (Pt), Palladium (Pd), and Rubindium (Rd)). However, those materials are expensive, high specific activity, limited supply, easily oxidized and easily broken

at temperature of 500-900 °C [3]. The cheaper ranges of oxides (CuO, V_2O_5, NiO, MoO_3, and Cr_2O_3) compared to precious metals are being investigated as alternative catalyst [3,4].

Ultrasonic is the technique to achieve finer surface structure and breaking the agglomerate. At low intensity, the wave will induce motion and mixing, a process called by acoustic streaming [5]. At higher intensities, ultrasonic propagated by oscillating pressure waves that alternately stretch and compress the liquid, thereby creating during expansion tiny micro bubbles or cavities which then collapse during compression. The ultrasonic frequencies which commonly performed for processing material between 16 kHz to 2 MHz where the sonochemistry principle is shown in Fig. 1.
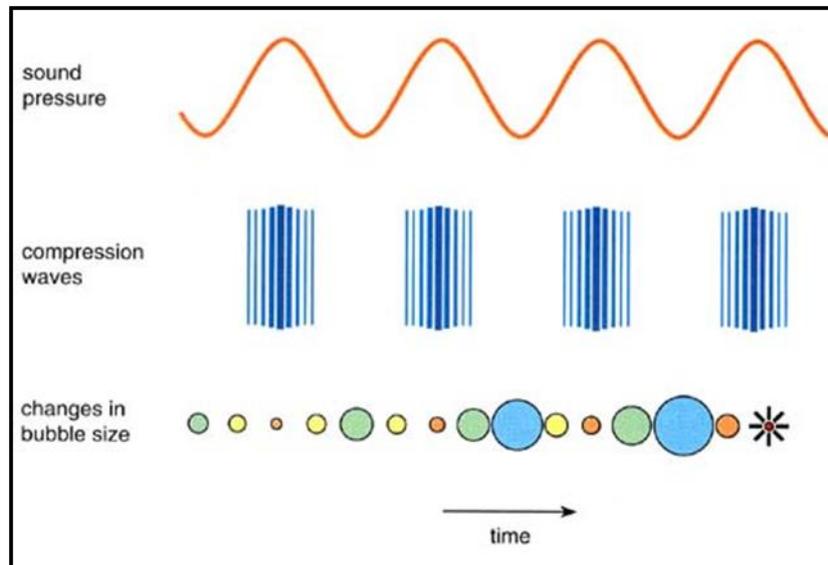
Fig. 1 - Principle of ultrasonic process [6]

Studied by Panin et al. [7] used the exciting ultrasonic oscilation by amplitude and frequency of 15 µm and 24 kHz within a treating tool and the other study that used the frequency of 25 kHz and 100 W, respectively for treating the surface of $Mg(OH)_2$ [8]. Ultrasonic bath was successfully investigated by Kim et al. [5] and Chandni and Arthur [9]. They used ceramic washcoat such as Al_2O_3 and γ-Al_2O_3 and metallic substrate is FeCrAl for CATCO development.

Some coating technology for coating the substrate has been investigated by previous researchers such as dip coating [10], co-precipitation, spray-pyrolysis and sol-gel methods [11], electrophoretic deposition [12], aluminizing technique [13] and Solution Combustion Synthesis (SCS) [14]. Those techniques are successfully conducted, however there are limitations in applying the catalyst in the powder form. Currently, electroplating technique is one of the most promising technique in coating technique. Electrodeposition process of hybrid coating was investigated by Wua et al. [15]. Electrodeposition material of Co–Ni–Al_2O_3 using sulphamate type of electrolyte is applied into the electroplating process where the effect of ratio on the composition, pH, morphology and magnetic properties of Co–Ni–Al_2O_3 thin film from a glycine bath is investigated. The results show that the appropriate condition to obtain a good coating by maximizing alumina content. Therefore, Al_2O_3 potential as electrodeposition material on FeCrAl substrate [16,17]. Moreover, γ-Al_2O_3 powder is more challenged to explore as coating material as investigated by Kim et al. [5]. In this research will be applied the FeCrAl substrate, γ-Al_2O_3 washcoat and NiO catalyst and it coated by combination technique between ultrasonic and electroplating that believe will be improve the CATCO properties in terms of high thermal stability due to protective oxide layer development during the coating process.

2. Research Methodology

The raw materials of this study were FeCrAl foils as substrate, γ-Al_2O_3 as a washcoat material, Nickel Oxide (NiO) plate and electrolyte solution. The FeCrAl that not performed by any coating activity was called by raw material. The FeCrAl and γ-Al_2O_3 that coated by ultrasonic bath was called by UB samples. The FeCrAl, γ-Al_2O_3 & NiO that coated by ultrasonic bath combined with electroplating technique was called by UB+EL samples. The FeCrAl, γ-Al_2O_3 and NiO that coated by electroplating technique was called by EL samples.

Ultrasonic bath, electroplating, combination of ultrasonic and electroplating were conducted to FeCrAl foil which cut in size of 40 mm x 20 mm and γ-Al_2O_3 powder. During ultrasonic process, the frequency of 35 kHz and various ultrasonic times of 1, 1.5, 2, 2.5 and 3 hours is imposed. Electroplating process is conducted through some components such as electrolyte, anti-pitting agent, anode and cathode. Sulphamate type which consists of nickel (ii) sulphate 6-hydrate ($NiSO_4.6H_2O$), nickel (ii) chloride ($NiCl_2·6H_2O$), boric acid (H_3BO_3), and sodium dodecyl sulfate

($C_{12}H_{25}OSO_3.Na$). A nickel (Ni) plate substrate acted as anode with the size of 50 mm x 10 mm, whereas a FeCrAl acted as cathode with the size of 40 mm x 20 mm. The distance between anode and cathode was adjusted at 25 mm. The electroplating was conducted for several variation times of 15, 30, 45, 60, and 75 minutes, current density of 8 A/dm^2, 3 g γ-Al_2O_3 inserted into the beaker for each sample and total surface area of 1600 mm^2 in two sides. Analysis that conducted in this research is Scanning Electron Microscope (SEM)-Electron Dispersive Spectroscopy (EDS) (JEOL, JSM-6380LA, Japan) for composition investigation. High Vacuum (HV) mode is used in SEM process with Secondary-Electron Image (SEI) detector will be emitted from inelastic collisions with electrons in the k-orbital of the specimen's atoms. Thermo Gravimetric Analysis (TGA) (LINSEIS, L81/1550, Germany) for investigating the thermal stability of coated and uncoated material that conducted at temperature of 1000 °C with heating rate and cooling rate of 100 °C per minutes. This temperature was performed due to the maximum temperature of exhaust emission system in gasoline engine in the range of 800-850 °C. The samples were measured by using microbalance with accuracy of 0.1 mg and then the samples put into TGA machine.

3. Results and Discussion

3.1 Composition Analysis

Composition analysis were performed on the coated FeCrAl by γ-Al_2O_3 powder and NiO catalyst using several methods such as Ultrasonic Bath (UB), Ultrasonic Bath + Electroplating (UB+EL) and Electroplating (EL) Technique. From EDS analysis was observed the composition of coated and uncoated FeCrAl. SEM and EDS characterization are performed after the coated and uncoated FeCrAl is heated at high temperature operation of 1000 °C that purposed to activate protective oxide layer and to eliminate the other chemical agent which embedded during coating process.

(a) Raw Materials and UB Samples

Composition analysis of FeCrAl substrate as raw material and coated FeCrAl by γ-Al_2O_3 powder using ultrasonic technique as listed in Table 1. Raw material mainly consists of three major elements of Fe, Cr and Al with Fe element was dominated for 74.13 wt%. The composition of UB samples mainly consists of Fe, Cr, Al, O and C due to FeCrAl substrate was deposited by γ-Al_2O_3 powder. In composition analysis, Fe and Cr were dominated in each sample for 60.52-65.13 wt% and 16.55-18.66 wt%. Therefore, the material has high temperature range operation. In UB samples C content was increased that caused by heating process after ultrasonic process to drain the samples from ethanol as electrolyte. Oxygen content also increase which caused by oxygen cavitation on the γ-Al_2O_3 coating layer which can approved by surface morphology analysis [16]. In addition, the increment of Al, Cr and Fe content because it activated by ultrasonic technique by collisions during the process and also because it has main components of FeCrAl fabrication.

Table 1 - Composition analysis of raw material and UB samples

Sample name	Elements (wt%)				
	C	O	Al	Cr	Fe
Raw	-	-	5.62	20.25	74.13
UB 1 h	13.45	4.6	4.87	16.55	60.52
UB 1.5 h	9.16	3.58	4.91	17.22	65.13
UB 2 h	9.91	3.03	4.61	18.60	63.85
UB 2.5 h	8.93	3.07	5.03	18.33	64.63
UB 3 h	9.15	4.38	4.94	18.66	62.88

The composition analysis of raw material and UB samples highly related with compound analysis that observed the several compound that developed during washcoat process. In UB samples has several compounds such as FeCrAl, FeO, γ-Al_2O_3 and $FeCr_2O_3$. FeCrAl and γ-Al_2O_3. That compounds increased the thermal stability by lower mass change as compared with raw material for 17.46 mg. This property will be given high impact on improving the CATCO endurance in exhaust emission system that operate in high temperature and extreme condition. According to Jung and Bae [18], the maximum range of exhaust temperature in exhaust emission system was ≤800 to 850 °C.

(b) EL Samples

Composition analysis of EL samples with various time of 15, 30, 45, 60, and 75 min as listed in Table 2. This technique was conducted by sulphamate type solution, NiO as anode and FeCrAl as cathode as well as γ-Al_2O_3 as coating material. The composition of EL samples mainly consists of 7 elements such as Fe, Cr, Al, O, C, Ni, and Na elements. The range of composition for each element was 52.56-63.54 wt% for Fe element, Al for 3.56-11.89 wt%, Cr

for 14.97-18.56 wt%, O for 2.47-11.78 wt%, C for 8.33-11.85 wt%, Na for 0.11-0.48 wt% and Ni for 0.17- 1.58 wt%. The element was dominated by Fe and Cr elements with high weight percentage in each sample. In addition, Na and Ni also present in EL samples which play the important role when the coated material is performed in high temperature of 1000 °C [19]. That data was approved by compound analysis that those elements develop some compounds such as FeCrAl, FeO, γ-Al_2O_3, $FeCr_2O_3$, NiO, $NiAlO_4$, $NiCr_2O_4$ and NaO_2. 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 O content will promote higher diffusion phenomena of the samples [20].

Table 2 - Composition analysis of EL samples

Sample name	Elements (wt%)						
	O	C	Al	Cr	Fe	Na	Ni
EL 15 min	2.47	11.85	3.56	18.43	63.04	0.48	0.17
EL 30 min	2.96	8.33	4.92	18.56	63.54	0.11	1.58
EL 45 min	5.2	10.75	4.13	16.47	62.66	0.28	0.52
EL 60 min	11.78	10.65	7.74	16.09	53.83	0.42	0.51
EL 75 min	10.46	9.23	11.89	14.97	52.56	0.14	1.03

Coating activity and coating layer believe has high diffusion of γ-Al_2O_3 to the FeCrAl substrate since there is cation and anion transport which led to higher diffusion coefficient [20]. The compounds that has been observed shown promising improvement on substrate properties in high thermal stability at high temperature application up to 1000 °C that supported by thermal stability analysis that EL samples has lower mass change of 3.99 mg as compared with raw material and UB samples that promote protective oxide layer on FeCrAl.

(c) UB+EL Samples

Combination of Ultrasonic and Electroplating Technique (UB+EL) has successfully performed to coat FeCrAl material by using γ-Al_2O_3 and NiO in order to develop more protective oxide layer in high temperature operation and long-term operation. UB+EL samples for various holding time of 15, 30, 45, 60, and 75 minutes as listed in Table 3. Elements that were observed after UB+EL technique such as Fe, Cr, Al, O, C, Ni, and Na elements. Therefore, based on compound analysis, UB+EL samples develop some compounds as protective oxide layer that consists of CrAl, FeO, γ-Al_2O_3, $FeCr_2O_3$, NiO, NaO_2, $NiAl_2O_4$ and $NiCr_2O_4$. The composition of UB+EL samples in the range of 55.95-60.63 wt% for Fe element, Al for 5.85-9.23 wt%, Cr for 16.33-19.54 wt%, O for 4.57-8.36 wt%, C for 8.8-13.43 wt%, Na for 0.03-0.55 wt%, and Ni for 0.17-0.62 wt%. Ni has developed because there is diffusion mechanism between Ni as anode and FeCrAl as cathode when Ni-electroplating process.

Table 3 - Composition analysis of UB+EL samples

Sample name	Elements (wt%)						
	O	C	Al	Cr	Fe	Na	Ni
UB+EL 15 min	8.36	9.95	9.23	16.33	55.95	0.41	0.25
UB+EL 30 min	5.49	13.43	6.03	16.59	57.88	0.03	0.62
UB+EL 45 min	5.32	10.41	6.37	17.9	58.84	0.55	0.6
UB+EL 60 min	5.22	12.51	5.85	17.35	59.16	0.09	0.17
UB+EL 75 min	4.57	8.8	5.93	19.54	60.63	0.32	0.22

Composition analysis of UB+EL samples shows the important of elements in the samples to increase the properties of material such as thermal stability due to compound development during the coating process. UB+EL samples has smallest mass change of 2.85 mg that indicated the material has highest thermal stability as compared with raw material, UB and EL samples.

3.2 Thermal Stability of Coated and Uncoated FeCrAl

Thermal stability analysis was conducted using Thermo Gravimetric Analysis (TGA) to investigate the effect of the treatment on the thermal stability in high temperature. Thermal stability is shown by low mass change while operated in high temperature of 1000 °C. Mass change of coated and uncoated FeCrAl substrate quite related to the mass change derivative because it shows the gradation and degradation mass in each temperature. Raw material shows

the highest mass change as compared with coated material which indicated that it has lowest thermal stability that caused by FeCrAl is unprotected by any oxide protective layer such as Cr_2O_3, FeO, NiO, and γ-Al_2O_3.
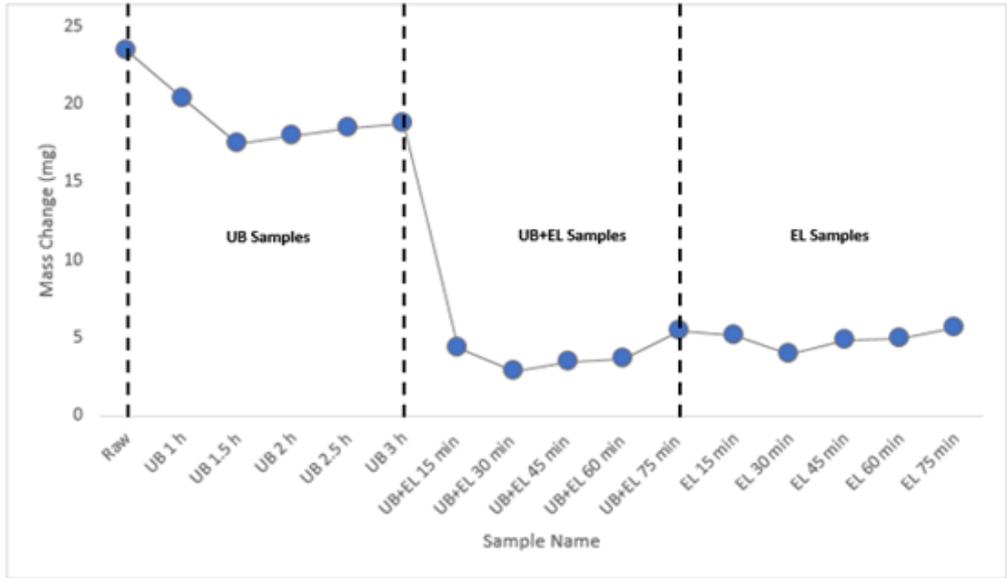
Fig. 2 - Mass change of coated and uncoated samples

The lowest mass change and highest mass change derivative of UB samples in each treatment is shown Fig. 2 and Fig. 3 were located at UB 1.5 h for 17.46 mg and 0.03760 mg/°C, for UB+EL 30 min samples 2.85 mg and 0.01000 mg/°C and for EL 30 min samples of 3.99 mg and 0.01000 mg/°C. Comparison between treatments regarding to the mass change and mass change derivative is shown that UB+EL 30 min sample has the lowest mass change and mass change derivative relatively high because it have a high protective oxide scale formed by inside diffusion of chromium (Cr^{2-}). It supported by compound analysis that UB+EL 30 min developed some compounds such as FeCrAl, FeO, γ-Al_2O_3, $FeCr_2O_3$, NiO, NaO_2, $NiAl_2O_4$ and $NiCr_2O_4$. The distribution of oxide scale in the sample is needed to improve the mechanical properties of coated FeCrAl substrate and to reduce the change effects of the material condition from ductile to brittle [21].

Fig. 2 shows that raw material has the highest mass change is compared with coated materials. The lowest mass changes as shown by UB+EL 30 min sample and followed by EL 30 min. Lower mass change is indicated that the material have higher thermal stability because high protective oxide scale based on EDS analysis such as FeCrAl, FeO, γ-Al_2O_3, $FeCr_2O_3$, NiO, $NiAlO_4$, $NiCr_2O_4$, and NaO_2 developed through this method. That compounds developed because reaction when ultrasonic treatment through its cavitation which make finer γ-Al_2O_3 coated layer and electroplating technique through reaction between anode and cathodes by sulphamate electrolyte.
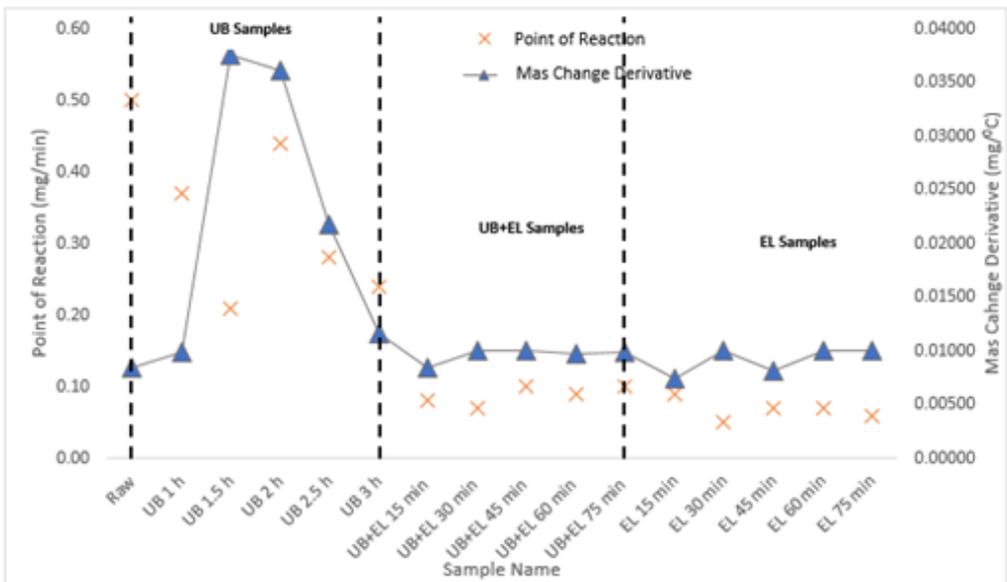
Fig. 3 - Mass change derivative and point of reaction of coated and uncoated samples

The unstable mass change derivative and point of reaction for all samples as shown in Fig. 3. There are gradation and degradation during the TGA analysis. First condition is the oxidation (gradation mass) of mass change derivative was observed when the compound formed by the reaction with oxygen or oxygen bonding has occurred. The mass change derivative has increased which occurs in temperature of 110.97-330.42 °C, 540.79-709.49 °C, and 793.87-878.29 °C. Second condition is the degradation of mass change derivative due to the decreasing oxygen bonding [22]. Degradation was occurred in range temperature of 331.42-498.69 °C and 879.29-960 °C, respectively.

4. Conclusion

The coating process by ultrasonic and electroplating was very effective to embedded the γ-Al$_2$O$_3$ washcoat and NiO catalyst on FeCrAl substrate that observed by SEM analysis. The coated samples were consisting of several elements and lead the increment of C, O, Al, Cr, Fe, Na, and Ni as compared with raw material. That increment causes the thermal stability increased as compared to raw material, where the lowest thermal stability observed by UB+EL 30 min for lowest mass change of 2.85 mg with point of reaction is 0.07 mg/min. It means that the coating technique by ultrasonic and electroplating very recommended to increase the thermal stability of CATCO material and promising CATCO material to replace the ceramic CATCO material.

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