Oxidation Resistance Analysis Of Metallic (FeCrAl Foil) Catalytic Converter Developed By Ultrasonic Approach

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Abstract. Mobile sources contribute about 44% of outdoor toxic emissions, approximately 50% of cancer risk and at around 74% of non-cancer risk health problems. Catalytic converter is quite needed in removing the pollutant and in preventing a health problem. The main problem in the catalytic converter is low oxidation resistance when operated at high temperature. Therefore, this paper aimed to develop catalytic converter material in high-temperature operation at around 1100 °C using FeCrAl foils as a metallic catalytic converter which coated by γ-Al2O3. This research is conducted using 3 various techniques such as ultrasonic bath for 3, 4, and 5 hours, Nickel (Ni) electroplating for 30, 45 and 60 minutes and the combination of ultrasonic bath and electroplating technique. Oxidation resistance analysis was conducted using tube furnace under argon gas for 60 hours in 3 cycles. Mass changes analysis of treated samples is showed by degradation mass. Lowest mass change of by ultrasonic bath samples is 0.3 wt%, for a combination of ultrasonic and electroplating samples is 0.3 wt% shown by UT 3 hours as well as 0.6 shown by EP 30 min. Parabolic rate constant is obtained by the time calculation based on the mass change of treated and untreated samples. It shown that UB 3 h is lowest parabolic rate constant of 2.258 x10-20 g2 cm-4s -1 and UB 5 h is 1.13 x10-20 g2 cm-4s -1. Lowest mass gain and lowest parabolic rate constant are become an indicator that the samples and that technique are recommended to fabricate the catalytic converter.

1 Introduction

Nowadays, there are many problems in our environment contributed by transportation sector especially from motor vehicle [1]. According to Malaysia Environmental Quality Report there are many types of pollutants which release by normal engine operation condition such as Carbon Monoxide (CO, 0.5 vol. %), Unburned Hydrocarbons (HC, 350 vppm), Nitrogen Oxides (NO_x, 900 vppm), Hydrogen (H_2, 0.17 vol. %), Water (H_2O, 10 vol. %), Carbon dioxide (CO_2, 10 vol. %), Oxygen (O_2, 0.5 vol. %). According to these data, HC, CO and NO_x are the major pollutants that influence to the outdoor toxic emission,

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cancer risk and non-cancer risk health problem [2,3]. They reaction are mentioned in Eq 1, 2 and 3 [4].

$$2CO + O_2 \rightarrow 2CO_2 \quad (1)$$

$$C_xH_{2x}+2 + [(3x+1)/2]O_2 \rightarrow xCO_2 + (x+1)H_2O \quad (2)$$

$$2NO_x \rightarrow xO_2 + N_2 \quad (3)$$

These three reactions occur most efficiently when the catalytic converter receives the exhaust gas from an engine running slightly above the stoichiometric point. In below of stoichiometric point shows the necessary mixing rate of the most common fuels [4].

The technology of vehicle emission reduction can be categorized into two major parts, namely primary and secondary method. For the primary method, it depends on fuel used by vehicle based on air treatment and combustion process. In the meantime, the use of a catalytic converter in the exhaust system of vehicles is the secondary method [4]. These studies focus on the catalytic converter as vehicle emission reduction by new treated material. There are 2 major material types for catalytic converter which are ceramic and metallic material. Generally, physical parameter of the catalytic converter is listed in Table 1.

Table 1. Physical Parameters of the Converter [5].

Physical parameters of the converter	
Wall density	2500 kg/m
Wall thermal conductivity	2 W/mK
Wall heat capacity	1400 J/kgK
Elective wall thickness	0.25mm
Thickness of washcoat layer	0.05mm
Porosity of washcoat	0.41
Channel hydraulic diameter	1.4mm
Channel open frontal area	1.96mm
Porosity of monolith	72%

First catalytic converter is developed using ceramic honeycomb substrate which based on cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ - 14% MgO, 35% Al_2O_3 and 51% SiO_2). That material is selected because they it has many advantages in softening points with higher attrition resistance, high melting, and lower pressure losses, low thermal expansion, high shock resistance as compared to pallet converter [6]. start from the 1970s, honeycomb substrate with ultra thin foil, corrugated and laid up is developed by ferritic steel which called by FeCr alloy. It consists of Iron (Fe), Chromium (Cr), Aluminum (Al) and Yttrium (Y). It protected by Alumina (Al_2O_3) in order to achieve the withstand high temperature and corrosive condition in exhaust [7]. Metallic and ceramic catalytic converter is shown in Figure 1.

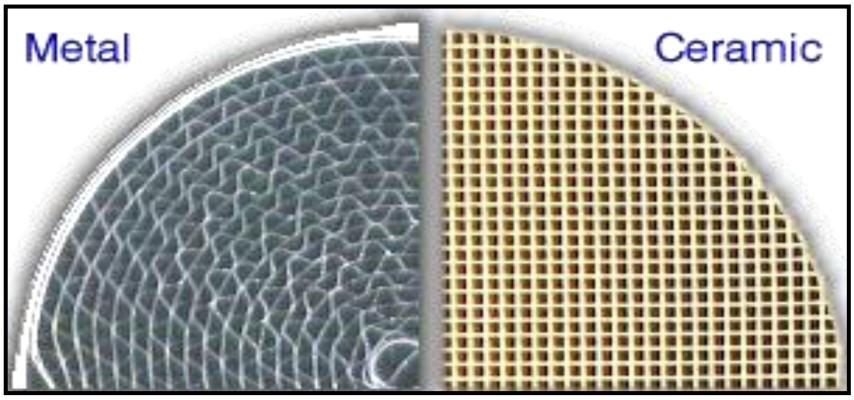

Fig. 1. Ceramic and metallic substrate converter [7].

The metallic catalytic converter has many promising properties such as high melting, high cell densities, high thermal shock resistance and low-pressure losses. But it has more advantages as compared to ceramic material in physical properties i.e. low specific heat and cheap (low-cost fabrication) [1]. Nowadays, FeCrAl is the promising metallic catalytic converter because it has excellent oxidation resistance at a high temperature of 1300 °C [8] and it commonly coated by γ-Al_2O_3 powders as corrosion and oxidation protective [9]. It used as coated material because the low price, good chemical stability, high micro-hardness and wear resistance at high temperature [10]. Other material such as Pt, Rh and Pd is not used in this research because it sensitive to thermal degradation at high temperature, CeO_2–Mn because it trapping of sulfur which led to corrosion [12].

Therefore, In this research is conducted using FeCrAL foil as substrate and γ-Al_2O_3 powders as wash coat material in order to achieve high oxidation resistance treated by ultrasonic approach. That treatment is chosen because during the ultrasonic process, high-speed bubbles producing a jet of liquid moving at around 100 m/sec. High velocity a jet potential to applied for cleaning, removing impurities from spent catalyst, electroplating or surface treatment process [13], and predicted to catalyst activation after and during coating process.

2 Methodology

Coating activity in this research is conducted using an ultrasonic approach which divided into three signed methods which are ultrasonic bath, nickel (Ni) electroplating and the combination of ultrasonic bath and electroplating technique. The material used in this research such as FeCrAl foil, γ-Al2O3, Ni plate, Nickel Sulphamate ($Ni(SO_3NH_2)2.4H_2O$), nickel chloride ($NiCl{\cdot}6H_2O$), boric acid (H_2BO_3), and sodium Lauryal Sulphate ($C_{12}H_{25}SO_4Na$) Natrium Hydroxide (NaOH).

2.1 Ultrasonic Bath Process

Ultrasonic bath technique is purposed to the preliminary coating process of γ-Al_2O_3 to FeCrAl foil. FeCrAl foil is being cut in the size of 30 x 15 mm. Ethanol with a concentration of 20g/l is used as coating media in order to accelerate the γ-Al_2O_3 ebbed into the FeCrAl foil. Ultrasonic bath process is conducted using frequency of 35 kHz in various times of 3, 4, and 5 hours. The mechanism of the ultrasonic bath is shown in Figure 2.

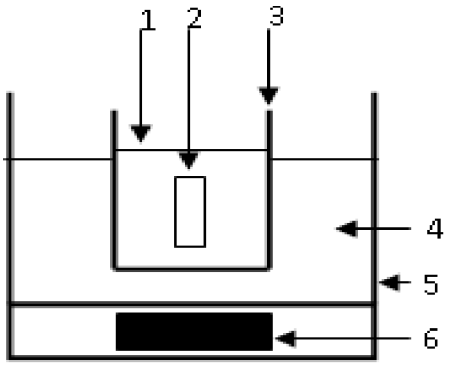

Fig. 2. Schematic diagram of ultrasonic cleaning bath (1) Ethanol; (2) FeCrAl; (3) Beaker; (4) Water; (5) Bath; (6) Ultrasonic source.

2.2 Nickel (Ni) Electroplating Process

In electroplating process, there are several components that are needed to be concern such as electrolyte (sulphamate type), anti-pitting agent, anode and cathode. The electrolyte is prepared by employing distilled water at a constant temperature of 60 °C and the adjustment of the pH value around 2.5-5.4 by manipulating the HCl and NaOH as the reagent. Ni plate is positioned as an anode and FeCrAl as the cathode with distance approximately of 25 mm with the current density of 2 A/dm^2 and total surface area of 450 mm^2. Illustration of the schematic diagram of the electroplating process is shown in Figure 3 and electroplating reaction is shown in Figure 4.

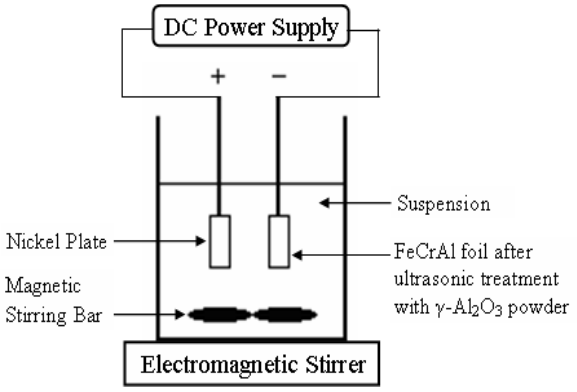

Fig. 3. Schematic diagram of electroplating process.

Fig. 4. The reaction occurs during electroplating.

2.3 Oxidation test

Tube furnace is held under argon gas environment at the temperature of 1100°C with heating and cooling rate of 5 °C/min, argon gas flow rate of 51 ml/min and flow density of 3.98 g/ml. The experiment was designed at 3 cycles and each cycle was carried out during 20 h of saturated period. Prior to, the material mass was measured by an electronic microbalance with the precision of 0.001g. After oxidation test, the data is measured by Eq. 3 and Eq. 4.

$$\Delta W = \frac{W_1 - W_1}{A_1} \tag{4}$$

Where;

Wt = Sample weight after each cycles of the oxidation process.
Wi = Initial weight sample
Ai = The surface area of the sample before oxidation process.

The calculation for the parabolic rate constant (kp) using parabolic rate law

$$\left(\frac{\Delta W}{A_1}\right)^2 = k_p t \tag{5}$$

Where;

t = The oxidation time (s)
k_p= The parabolic rate constant ($g^2\ cm^{-4} s^{-1}$)

3 Result and Discussion

3.1 Mass Changes

Mass change analysis is used to observe the oxidation resistance or thermal stability of the material. the effectiveness of the method to improve the oxidation resistance is signed by small mass change. Mass change of the ultrasonic bath and combination of ultrasonic and electroplating technique samples is listed in Table 2. It shows that the smallest mass change is signed by UB 5 hours in 3rd cycles with no mass change observed compared to UB 3 and 4 hours with 0.3 wt% mass change in every step. For UT samples show that different pattern with UB samples where the UT 5 hours shows the highest mass change of 2.167 wt% as compared to UT 3 hours of 0.3wt% and UT 4 hours of 0.9 wt%. Longer time of

ultrasonic bath technique is led to the higher amount of γ-Al_2O_3 which embed in FeCrAl foil. γ-Al_2O_3 layer is proposed heat resistance before it spread into the FeCrAl foil. That phenomenon is not valid when the ultrasonic bath is combined with electroplating technique. It maybe caused by different liquid media where the ultrasonic bath use ethanol and electroplating use sulphamate type as solution. Different concentration is given high impact to the process of γ-Al_2O_3 to embed into FeCrAl foil.

Table 2. Mass changes of treated and untreated samples.

The mass of sample after oxidation test for ultrasonic bath sample (UB)			
	Mass change of UB for 3 Hours	Mass change of UB for 4 Hours	Mass change of UB for 5 Hours
Initial	0.319g	0.325g	0.32g
Cycle 1	0.319g	0.325g	0.32g
Cycle 2	0.318g	0.324g	0.319g
Cycle 3	0.317g	0.323g	0.319g
The mass of the sample after the oxidation test for ultrasonic bath followed by electroplating sample (UT)			
Initial	0.311g	0.327g	0.323g
Cycle 1	0.310g	0.327g	0.323g
Cycle 2	0.309g	0.324g	0.316g
Cycle 3	0.308g	0.321g	0.314g

The main coating process of this research is using Nickel electroplating technique. It aimed to improve the surface properties of FeCrAl by coating γ-Al2O3 such as to improve wear resistance, corrosion protection and oxidation resistance. This research is focused on developing high oxidation resistance of the treated FeCrAl sample which approved by small mass change after electroplating like shown in Figure 5.

Mass change analysis of treated samples shows the improvement properties high-temperature operation of 1100 °C. Electroplating (EP) for 30 minutes shown highest oxidation resistance by smallest mass changes of 0.6 wt% as compared to EP 45 min of 15.34 wt% and EP 60 h of 13.92 wt%. in these case, the mass changes increase linearly with the electroplating times. EP 30 min have higher deposition rate which provides uniformity of coating thickness and compact deposit are synthesized in template-based structure.

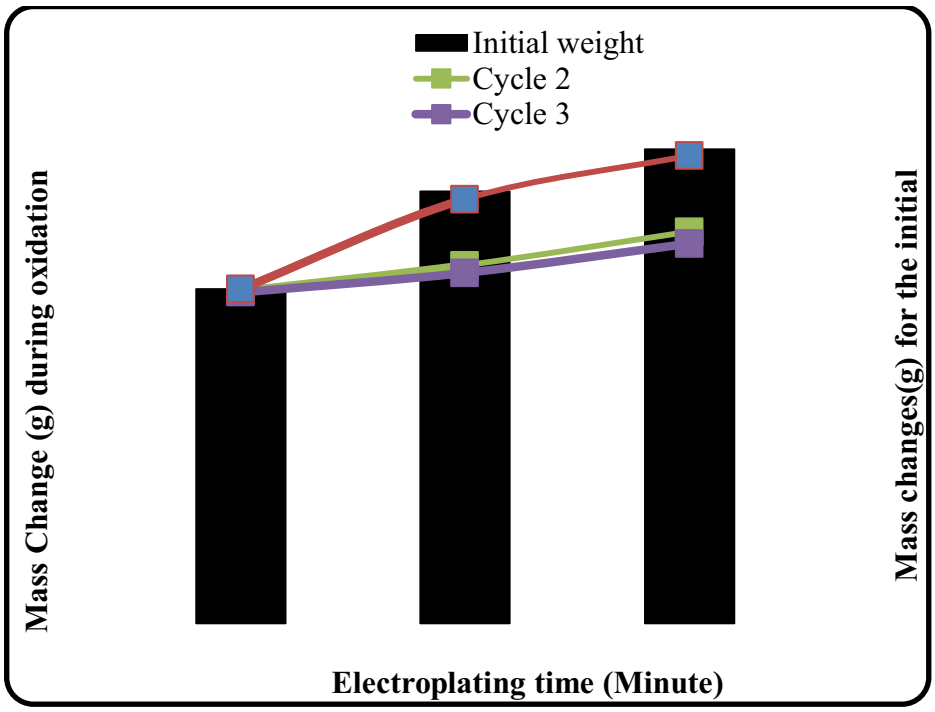

Fig. 5. Mass change of treated and untreated samples after electrodeposition process.

3.2 Parabolic Rate Constant

The parabolic rate constant is an intrinsic property of an oxidation resistant and normally used to measure its oxidation resistance. The parabolic rate constant of treated and untreated samples is listed in Table 3. Preliminary coating by UB 3 hours is obtain 2.258 x10-20 g^2 $cm^{-4}s^{-1}$ which compared to UB 4 (9.14 x10-09 g^2 $cm^{-4}s^{-1}$) and 5 hours (1.13 x10-20 g^2 $cm^{-4}s^{-1}$). The samples after a combination of ultrasonic bath and electroplating which signed by UT samples shown inline phenomena with UB samples. Where the UT 3 h shown lowest parabolic rate constant of 3.387 x10-20 g^2 $cm^{-4}s^{-1}$) as compared to UT 4 h (1.829 x10-18 g^2 $cm^{-4}s^{-1}$) and UT 5 h of (2.729 x10-17 g^2 $cm^{-4}s^{-1}$). Smallest mass change of EP 3 h effect to the lower parabolic rate constant for 7.968 x10-14 g^2 $cm^{-4}s^{-1}$) and higher kp shown by EP 4 h (4.27 x10-13 g^2 $cm^{-4}s^{-1}$) and EP 5 h (1.89 x10-12 g^2 $cm^{-4}s^{-1}$). All the results shows that 3 hours treatment times is most effective by ultrasonic bath, electroplating and combination of ultrasonic and electroplating technique.

Parabolic rate constant is remarkably reduced in 3 hours treatment times by spinel protection coating because it provided by γ-Al_2O_3 oxide scale. From the results of oxidation test that coated material shown an excellent resistance against the spallation and cracking which resulted by lower mass change and lower parabolic rate constant. Spalling and cracking phenomena commonly due to the oxide of coefficient of thermal expansion is mismatching [16].

Table 3. The parabolic rate constant for an ultrasonic bath.

Treatment	Average ($g^2\ cm^{-4} s^{-1}$)
UB 3Hours	2.258×10^{-20}
UB 4Hours	9.14×10^{-09}
UB $_{5Hours}$	2.258×10^{-20}
UT 3Hours	3.387×10^{-20}
UT 4Hours	1.829×10^{-18}
UT 5Hours	2.729×10^{-17}
EP 3Hours	7.968×10^{-14}
EP 4Hours	4.27×10^{-13}
EP 5Hours	1.89×10^{-12}

3.3 Statistical analysis

Statistical analysis is performed for all method in order to investigate the significance of parameter which applied in this research. Analysis of Variance (ANOVA) single factor is used to analyze the data. For electroplating results (Table 4) shows that the Fcrit of 4.066181 is bigger than F of 1.041539 means that this method is significant in changing the properties. Current density, sulphamate type, pH, and electroplating times give high effect to the improving oxidation resistance in high temperature of 1100 °C.

Table 4. Statistical analysis of after electroplating process (EP).

Source of Variation	*df*	*MS*	*F*	*F crit*
Between Groups	3	0.002496	1.041539	4.066181
Within Groups	8	0.002397		
Total	11			

Ultrasonic bath (Table 5) and the combination of ultrasonic bath and electroplating (Table 6) shown that the parameter conducted in those process is a significant effect to the oxidation resistance properties. It approved by statistical analysis which mentions that value of Fcrit>F. Ultrasonic bath obtains Fcrit of 4.120312 and F of 0.130165 meanwhile for UT samples obtain Fcrit of 4.066181 and F of 0.411606. When the ultrasonic bath is conducted, shock out wave through the liquid cause high-speed collision which promote micro coating occur on the FeCrAl foil.

Table 5. Statistical analysis of after ultrasonic bath technique (UB).

Source of Variation	*df*	*MS*	*F*	*F crit*
Between Groups	3	1.5E-06	0.130165	4.120312
Within Groups	8	1.15E-05		
Total	11			

Various groups in this research is divided into 4 such as Initial, cycle 1, cycle 2 and cycle 3 groups which have the same value of the df of 3 and 8. The standard deviation of all data in every group and every method show the differences which indicated that the fluctuate condition when oxidizing in temperature of 1100 °C occurs. The SD of UB initial is 0.0019, cycle 1 is 0.0019, cycle 2 is 0.0019 and cycle 3 is 0.0018. The SD for UT samples initial is 0.0048, cycle 1 is 0.0051, cycle 2 is 0.0043 and cycle 3 is 0.0038. The SD for EP samples initial is 0.0382, cycle 1 is 0.0362, cycle 2 is 0.0159 and cycle 3 is 0.0131. High standard deviation means that the data that resulted by the parameter is more significant effect as compared to lower standard deviation. However, all methods is recommended to produce the catalytic converter material with high oxidation properties.

Table 6. Statistical analysis of after combination of ultrasonic bath and electroplating (UT).

Source of Variation	*df*	*MS*	*F*	*F crit*
Between Groups	3	2.54E-05	0.411606	4.066181
Within Groups	8	6.18E-05		
Total	11			

4. Conclusion

FeCrAl was coated by γ-Al_2O_3 using 3 various methods and it can be concluded that the coated material has higher oxidation resistance as compared to the uncoated material. The smallest mass change of coated material is 0.3 wt% for UB 3 h and UT 3 h and 0.6 wt% for EP 3 h. Parabolic rate constant is linear with mass change value. The significance data is approved by statistical analysis for all the data shown that Fcrit>F. Consistency data is established that all parameter and all procedure that conducted in this research is in-line with the fundamental methods.

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