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**ALUMINUM OXIDE FORMATION ON FECRAL CATALYST SUPPORT BY ELECTRO-CHEMICAL COATING**

**POWSTAWANIE TLENKU GLINU NA NOŚNIKU KATALIZATORA FeCrAl PRZEZ OSADZANIE ELEKTROCHEMICZNE**

FeCrAl is comprised essentially of Fe, Cr, Al and generally considered as metallic substrates for catalyst support because of its advantage in the high-temperature corrosion resistance, high mechanical strength, and ductility. Oxidation film and its adhesion on FeCrAl surface with aluminum are important for catalyst life. Therefore various appropriate surface treatments such as thermal oxidation, Sol, PVD, CVD has studied. In this research, PEO (plasma electrolytic oxidation) process was applied to form the aluminum oxide on FeCrAl surface, and the formed oxide particle according to process conditions such as electric energy and oxidation time were investigated. Microstructure and aluminum oxide particle on FeCrAl surface after PEO process was observed by FE-SEM and EDS with element mapping analysis. The study presents possibility of aluminum oxide formation by electro-chemical coating process without any pretreatment of FeCrAl.

*Keywords:* FeCrAl, Catalyst support, Aluminum oxide formation, PEO (Plasma electrolytic oxidation), Electro-chemical coating

**1. Introduction**

Steam Methane Reforming (SMR) process is one of production of hydrogen gas using methane for energy saving. Aluminum oxide is usually used as commercial catalyst in SMR reactor, has severe endothermic reaction depend on mass transfer resistance. However, this ceramic pellet has low heat transfer and geometric surface area, so SMR reactor performance such as pressure, thermal shock resistance, and volumetric efficiency is decreased. For solving these problems, porous metal has developed as catalyst because of high heat transfer, geometric surface area, and superior mechanical properties.

FeCrAl is general Ni-Al<sub>2</sub>O<sub>3</sub> catalyst support because of its mechanical properties, though many studies have been tried to overcome FeCrAl-Al<sub>2</sub>O<sub>3</sub> interface adhesion problem by thermal expansion between FeCrAl and ceramic catalyst [1]. High temperature thermal oxidation, washcoat, and its combined process are representative method to have alumina oxide layer on FeCrAl [2-3]. Electroplating process also tried to obtain aluminum oxide layer on FeCrAl after thermal oxidation [4]. This study was carried out another approach by electro-chemical coating process for Al<sub>2</sub>O<sub>3</sub> layer formation on FeCrAl support without any pretreatment.

**2. Experimental**

The chemical composition of FeCrAl foil Kanthal D used in this study is shown Table 1. The FeCrAl foil (thickness 2

mm, width 8 mm) was cut to size (150 mm × 8 mm), and cleaned by ethanol in ultrasonic system and dried in oven at 80°. To observe Al<sub>2</sub>O<sub>3</sub> particle on FeCrAl surface, PEO

TABLE 1

Chemical composition of FeCrAl

|                     | C %  | Si % | Mn % | Cr % | Al % | Fe % |
|---------------------|------|------|------|------|------|------|
| Nominal composition |      |      |      |      | 4.8  | Bal. |
| Min                 | -    | -    | -    | 20.5 | -    |      |
| Max                 | 0.08 | 0.7  | 0.5  | 23.5 |      |      |

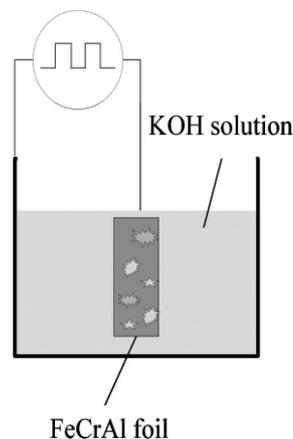


Fig. 1. A Schematic diagram of the plasma electrolytic oxidation process

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Test condition of electro-chemical oxidation on FeCrAl by plasma electrolytic oxidation

| Sample | Voltage (V) | Frequency (Hz) | Time (min) | Electrolyte | Mole ratio (mM) | Micro-arc charging |
|--------|-------------|----------------|------------|-------------|-----------------|--------------------|
| A      | 200         | 60             | 5          | KOH         | 10              | X                  |
| B      | 350         | 60             | 5          |             | 20              | X                  |
| C      | 400         | 60             | 5          |             | 20              | O                  |
| D      | 450         | 60             | 5          |             | 20              | O                  |
| E      | 450         | 60             | 10         |             | 20              | O                  |

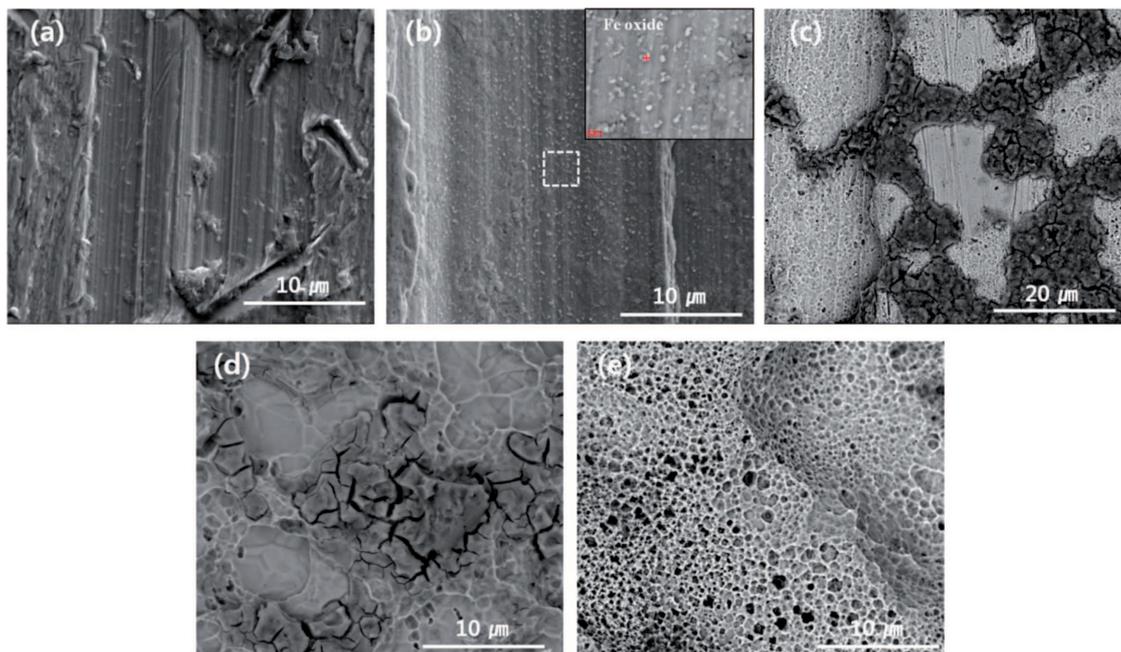


Fig. 2. Surface SEM microstructure image of FeCrAl : (a) bare sample, (b) sample B, (c) sample C, (d) sample D and (e) sample E

treatment was carried out on FeCrAl in an aqueous solution containing potassium hydroxide, using different voltages from 200 V to 450 V. Fig. 1 shows the schematic of PEO process in this study. Detail experiment condition is shown Table 2. After finishing PEO process, microstructure of each FeCrAl sample surface was observed with the high resolution scanning electronic microscope (HR FE-SEM) models Nova Nano 200 (FEI Co., Ltd. USA). Aluminum oxide particle on FeCrAl surface produced from the PEO process was analyzed EDS and mapping.

### 3. Results and discussion

Fig. 2 shows the each tested sample microstructure of the PEO coating. Fine porosity area was observed in the edge area of sample A and B after PEO process. The micro arc charging was observed clearly when the applied voltage was over 400 V. The surface of bare FeCrAl foil has longitudinal extruded mark in Fig. 2(a). The fine Fe oxide particle was observed in center area of sample B surface (Fig. 2(b)). The fine particle came from the weak area from the Fe based oxide film which

was generated in the electrolyte, and the oxide film would be broken down after applied voltage exceeded 350 V.

The PEO coating surface has fine scale porosity, crack, and dimple microstructure in sample C, D, and E. Qingbiao Li et al. reported the molten oxide and gas bubbles from plasma discharge channels was main reason to create micro pore and thermal stress from rapid solidification of the molten oxide in electrolyte caused crack formation [5]. This microstructure on the surface of the PEO coatings can be defect aspect of adhesion with Ni-Al<sub>2</sub>O<sub>3</sub> catalysis.

The dark oxidation area on FeCrAl surface was distributed and increased with increase applied voltage in sample C and D. Fig. 3 shows the comparison of elements weight percent of each sample by EDS analysis. In this analysis most of the oxidation elements was Fe, Cr and O. Fe content is predominant element in FeCrAl substrate, therefore Fe oxide foam deposited on FeCrAl in PEO process.

At the same time Al and O contents tended to increase while Fe and Cr contents decreased gradually according to increase applied voltage. Fig. 4 shows some Al oxide area was observed in the FeCrAl surface center in sample D. This small part of Al oxide foam was left from the initial weak oxide film, fallen out by applied voltage during PEO process. It shows that

the oxide composite area increased with enhance of reactivity between insulating oxide film layer and micro-arc charging in electrolyte by applied more high energy than other samples. In addition ionization of Al which has more high ionization tendency than Fe and Cr is accelerated. Consequently bonding energy with  $O^-$  from electrolyte is increased, and much Al contents exist as oxide form relatively. Although homogenous alumina oxide dispersion was not observed and needed additional evaluation such as adhesion with interface of FeCrAl surface, Al oxide could be formed by PEO process without thermal oxidation or sol coating process. On the other hand, Al and O contents decreased with increase of oxidation time in sample E. This result shows that partial oxide form with Al contents was eliminated according to increase of oxidation time and many fine plasma discharge channels formed on FeCrAl surface (see Fig. 2(e)).

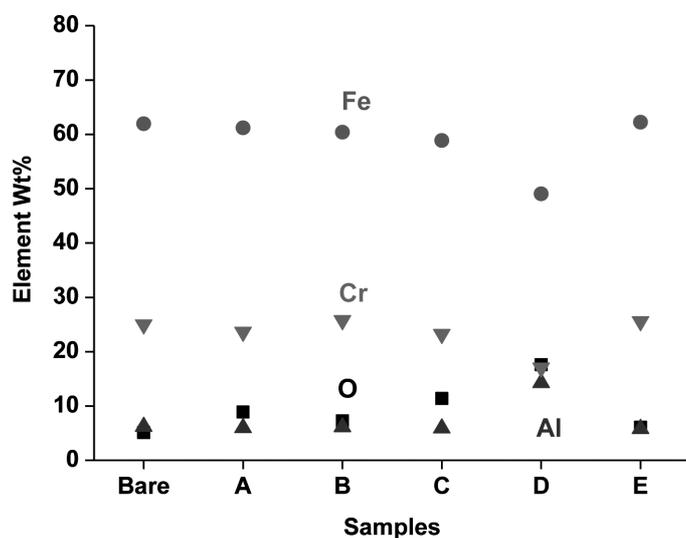


Fig. 3. Comparison of the element weight percent by EDS analysis

For the development of porous metal catalyst and enhancement the catalyst performance, this study proposed a new oxidation method and confirmed partial of  $Al_2O_3$  formation on FeCrAl catalyst support by PEO process. There are still some problems to be solved and needed theoretical study that homogenous  $Al_2O_3$  composition dispersion with refinement of the Al ions diffusion control by micro-arc charge condition such as appropriate voltage and current density control, electrolyte selection, and cooling condition, understanding the  $Al_2O_3$  formation mechanism, and adhesion test with interface among Ni- $Al_2O_3$  catalysis layer, Fe/Al oxide form, and FeCrAl surface.

#### 4. Summary

Aluminum oxide formation on FeCrAl surface without any pretreatment by PEO process was investigated. Al and O contents increased and Al oxide area was observed when applied energy increased because of enhancement of reactivity between insulating oxide and micro-charging in electrolyte. More application and experiment to achieve homogenous  $Al_2O_3$  dispersion and coating by electro-chemical oxidation without several treatment stages such as thermal oxidation, sol coating etc will be carried out continuously. It can be expected that reduction of process energy and cost reduction, and in the SMR plant.

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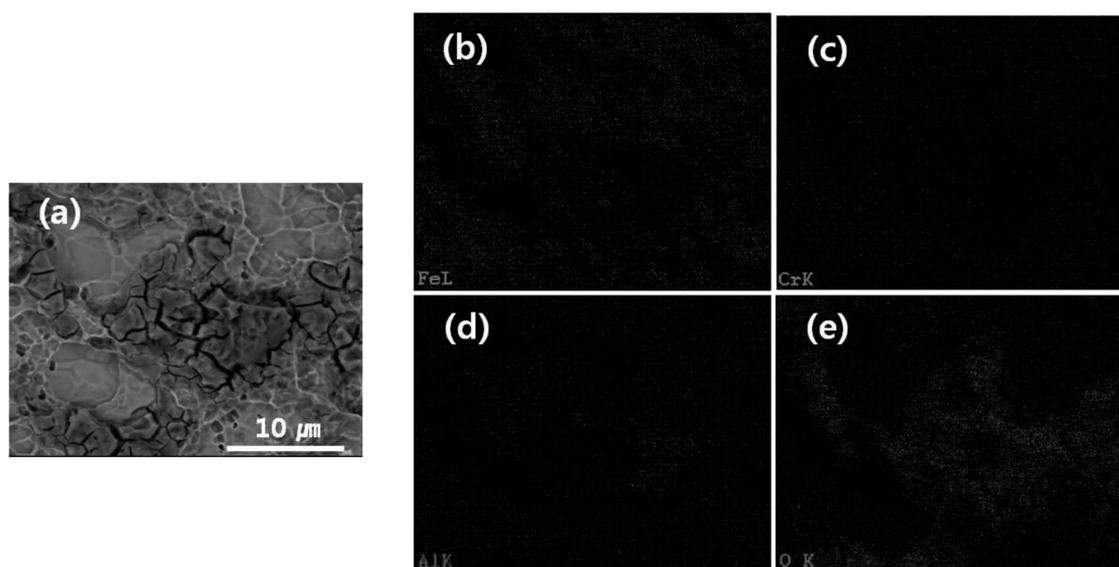


Fig. 4. Mapping analysis of FeCrAl surface in sample D : (a) BSE image of FeCrAl surface in sample D, (b) Fe-rich area, (c) Cr-rich area, (d) Al-rich area and (e) O-rich area

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