



Effect of La modification on the stability of coating alumina layer on FeCrAl alloy substrate



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ABSTRACT

In this work, better washcoating technology on a FeCrAl alloy support was studied, and the improving factors towards optimal coating were attained with regard to alumina primer. Surface La-modification of alumina stabilized the metastable phase of Al_2O_3 by inhibition of α -transformation leading to the maintenance of high surface area at temperatures of up to 1200 °C. Newly developed two step modification in 2 mol% La-modified Al_2O_3 resulted in better slurry with regard to surface charge as colloid dispersion and rheological properties under stress vs. shear rate condition. Surface La_2O_3 was able to control zeta potential to high pH region so that alkaline solution was applied to metallic substrate. The layer from a suspension coat process using the present alumina was morphologically stable without strong cracks, and maintained the surface area of 70 m^2/g , even when it was subjected to high temperatures of up to 1200 °C. The surface area of the dried slurry becomes lower than that of the coated layer after heat treatment in the case of 1 mol% La-modified Al_2O_3 , while in 2 mol% La-modified Al_2O_3 this negative influence was not found. The present coat layer effectively reacts with alumina interlayer grown on FeCrAl alloy edge by oxygen bulk diffusion and bonded into porous topcoat layer without heavy phase transformation. Surface La-modification of alumina induced better composite structure of both porous coat layer and strong bonding with alloy substrate.

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1. Introduction

Catalyst layers on metallic surfaces are becoming one of the most important coating technologies in developing structures such as metallic honeycombs and microreactors. Pressure drop and thermal and mechanical resistance become often serious issues in catalytic reactors, and metallic honeycombs (monoliths) are the useful option in severe conditions, e.g., automotive catalyst converters with cold start and exhaust velocity fluctuation [1–4]. Many methods can be used to deposit an active catalyst layer on a surface, which depend on the properties of the substrate surface and the catalyst that has to be deposited. Also structured catalysts and reactors become important for fuel processing, gas–solid synthetic reactions and environmental soluble process. They often require a shaping of the thin and porous catalyst layer on substrate, because of mass and/or heat transfer improvement [5].

Concerning the deposition on metallic monoliths, slurry impregnation is often used to deposit a catalytic active phase, so-called the wash-coat, because of inexpensive fabrication cost and wide selection of catalytic composition [6]. Materials and processing viewpoints are allowed to increase the adherence of the alumina and metal oxide

layer on the metallic support and thermal stability of the layer itself. Several factors are the interface microstructure fabricated by combination of methods given by rheology of slurry, the coating procedure followed by thermal oxidation of alloy, and thermal sintering of primer deposited powder layer [7–12]. In detail, the wash-coating technique must allow obtaining coatings on most metallic surfaces with the required homogeneity, amount loaded and adhesion provided that the metallic surface properties and the coating procedure including excess elimination and, in particular, the properties of the catalyst slurries are well controlled often using an alumina suspension [13–20].

This work examines the impact of a primer (alumina) material parameter controlling the coating of FeCrAl alloy metallic monoliths by studying thermal stabilized alumina with lanthanum (La) through focusing on the microstructural development of sintered layer and alumina/alloy interface. In general, to control stable layer of alumina, the stabilizer (element) doping technique to alumina support was applied. To achieve thermal stability of alumina coat layer, La is often used as modifier, because La-added alumina has the capability to keep high surface area under extremely heat condition [21–27]. Commercially available alumina is La-added transition alumina, in which a small amount of La is doped in alumina phase, i.e., a metastable crystal structure is stabilized by La_2O_3 . Surface characters of particles used for layer fabrication process should strongly affect both coating process and resultant interface between substrate and layer. La is one of the basic

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metal oxides to bring characteristic surface charge in water and oxidative surface of alloy at interface, and in addition high thermal stability to inhibit phase transition. Concerning the coating material characteristic in our paper, the surface La_2O_3 is surrounded on alumina surface by the impregnation technique of La. The aim of this work is to examine effect of surface modification especially surface La added on alumina powders, which was newly developed, in the coating technology of forming wash-coat layer on FeCrAl alloy substrate.

2. Experimental

2.1. Materials

FeCrAl alloy foils (Fe 72%, Cr 23% and Al 5%, 0.10 mm thickness) were used as coated substrates for alumina wash-coatings applied in rheological process in this work. All foils were cleaned at room temperature in acetone with ultrasonic vibration for 5 min, and then dried in air at 80 °C for 10 min. Pure $\gamma\text{-Al}_2\text{O}_3$ powders TA1301 (Al_2O_3 : $d_{50} = 4 \mu\text{m}$, BET specific surface area (SA) = 120 m^2/g) and 1 mol% La-modified $\gamma\text{-Al}_2\text{O}_3$ powders TA2301 (1La- Al_2O_3 : $d_{50} = 5 \mu\text{m}$, BET SA = 115 m^2/g) were supplied by Sumitomo Chemicals Co. (Japan). 2 mol% La modified $\gamma\text{-Al}_2\text{O}_3$ (2La- Al_2O_3 : $d_{50} = 6 \mu\text{m}$, BET SA = 112 m^2/g) was prepared by the impregnation of aqueous lanthanum(III) nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Wako Chemicals, >99%) to TA2301 powders. Previous studies have indicated that the surface area stabilization for powder appeared most effectively in 1 to 2 mol% La content as modifier to $\gamma\text{-Al}_2\text{O}_3$ [22–25].

2.2. Coating procedure

Slurries were prepared using the standard procedure in a mortar grinder with each powder-suspension batch. Aqueous suspensions of alumina with 4.8 vol.% (15 wt.%) were prepared with deionized water at room temperature, and then ammonia solution was added to prepare pH = 9.0 for the alumina suspension. Although coating slurries were made with different characteristics such as various solid contents and pH values, final slurry of desired solid content was mainly the condition achieved without inorganic and organic additives in this work. For the preparation of the coatings, pretreated metal foils were immersed into the slurry for 30 s, and then withdrawn using automatic dip-coating apparatus (dip coater MD-0408-S5, CDI Japan) under a steady rate of 0.1 to 10 mm/s, followed by the elimination of the excess without procedure (practically no excess slurry on substrate in the present condition). Although we applied many conditions of solid concentration, a withdrawing rate as well as pH of solution, a final condition about dip-speed was set to 3.9×10^{-3} m/s using the present slurries. An as-dipped coating sample was dried in atmosphere one night and then in an oven at 110 °C for 1 h in air and subsequently heated at 500 °C for 1 h in air. In order to compare microstructures of the coating films, powders and dried slurries that submitted to the same heat history, they were heated at elevated temperatures of up to 1300 °C for 3 h in air, respectively.

2.3. Characterization techniques

The property of suspension was monitored by a rheometer apparatus (MR500, UBM, Japan). Shear dependent stress behavior of the slurries under various shear conditions was evaluated by ascending and descending shear rate ramps in the range from 0 to 80 s^{-1} in 5 min, and from 80 to 0 s^{-1} in 5 min, respectively. The zeta potentials and zero charge point (pH) of powders in suspensions used for coating procedure were evaluated using the measurement of the ultrasonic vibration potential (UVP) apparatus (Pen-Kem, system 7000, USA).

Scanning electron microscopy (SEM, JEOL-JSM 6200, Japan) was used to observe the morphology of coated layers. The deposited layers directly impregnated to the substrate were observed on surface and cross-section after heat treatment. In order to form sample in which an anchoring sites at interface between substrate and deposited layer,

surface ultrasonic treatment was applied under condition in an ultrasonic vibration cleaner (WT-1200, Honda Denshi Co., Japan) with a power of 110 W and a frequency of 25 kHz for 60 min. Chemical elementary line and spot analyses at cross-section in coated samples were performed by an EDS detector attached in SEM apparatus. Before analysis, the sample was set in resin solution followed by polymerization, and then polished with the direction to cross-section.

Powder X-ray diffraction (XRD) apparatus (Rigaku Rint2200, Japan) with Cu-K α X-ray source (25 kV–30 mA) was used for the characterization of phases formed in samples after heat treatment at various temperatures. The surface areas of powders and coated layers were measured by the BET method at 77 K by N_2 adsorption (Tristar, Micrometrics, USA) after pretreating them at over 200 °C.

3. Results and discussion

3.1. Effect of La-modification on alumina

Figs. 1, 2 and 3 compare the XRD powder patterns of pure Al_2O_3 , 1La- Al_2O_3 and 2La- Al_2O_3 heated at various temperatures of up to 1300 °C for 3 h in air, respectively. The sequence of structural transformation of gamma alumina phase is simply as follows: $\gamma\text{-Al}_2\text{O}_3 \rightarrow (\theta\text{-Al}_2\text{O}_3) \rightarrow \alpha\text{-Al}_2\text{O}_3$, where $\theta\text{-Al}_2\text{O}_3$ did not appear in this work. In general, since the phase transformation of transition alumina to $\alpha\text{-Al}_2\text{O}_3$ phase (α -transformation) induces the rapid loss of surface area with grain growth, the inhibition of this transformation corresponds to an improvement of the thermal stability as a catalytic layer [23,24]. The XRD showed a larger amount of $\alpha\text{-Al}_2\text{O}_3$ for pure alumina than two La-modified aluminas at 1200 °C. When La-modification was applied, γ -phase of alumina was stabilized even around 1100–1200 °C, although a small amount of LaAlO_3 appeared above 850 °C for excess La doping. Depending on the increase of La doping amount, Figs. 1 and 2 showed that LaAlO_3 phase practically increased in 2 mol% La- $\gamma\text{-Al}_2\text{O}_3$, compared with 1La- Al_2O_3 . Thus, it is expected to realize heat-stability as support if 1La- or 2La- Al_2O_3 is used as a coat layer primer even subjected to operation around 1100–1200 °C because of the effective inhibition of α -transformation. Although the most heat-stable

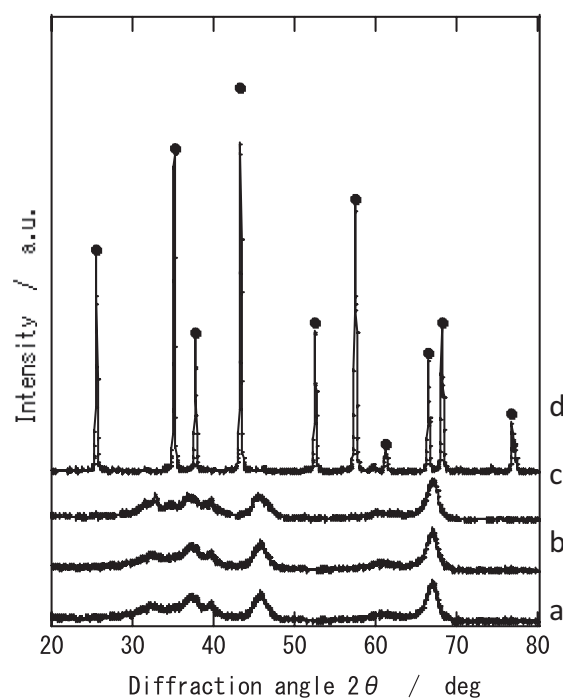


Fig. 1. XRD patterns of $\gamma\text{-Al}_2\text{O}_3$, heated at (a) 600 °C, (b) 800 °C, (c) 1100 °C, and (d) 1200 °C for 3 h in air. (●): $\alpha\text{-Al}_2\text{O}_3$.

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