

## Influence of $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ solid solution on depositing *g*-alumina washcoat on FeCrAl foils

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**Abstract.** The influence of  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution on properties of *g*-alumina based washcoat on FeCrAl foils was investigated. FeCrAl foils were pretreated at 950°C in air for 10 h before coating washcoat. Different amounts of  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution were added into  $\gamma$ -alumina-based slurries. The properties of washcoats were measured by ultrasonic vibration and thermal shock test, SEM, BET and XRD. The results show that the addition of  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution into slurries can improve *g*- $\text{Al}_2\text{O}_3$ -based washcoat adhesion on FeCrAl foils. The more the  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution added into slurries, the higher was the specific surface area of aged samples. XRD characterization proved that ceria–zirconia solid solution can inhibit the transformation of *g*- $\text{Al}_2\text{O}_3$  crystal into others at 1050°C for 20 h.

**Keywords.** Metallic substrates; *g*-alumina; washcoat; Ce–Zr solid solution.

### 1. Introduction

Recently, more rigorous regulations are forcing catalyst manufacturers to device new technologies in order to ensure a high catalytic activity. The usage of metallic substrate replacing ceramic substrate became one such improvement.

Metallic substrate, due to its high thermal conductivity and good ductility, has been found to be a preferred choice of catalyst substrates in applications where robust heat transfer, complicated flow path, and light weight are critically important (Vatcha 1998; Tronconi and Groppi 2000; Cerri *et al* 2001). However, there exists a problem that the metallic substrate and ceramic washcoat have different thermal expansion coefficients, which cause weak coating adhesion. To compensate the intrinsic disadvantages, some pretreatments have been presented. Adomaitis *et al* (1996) carried out a precoating treatment to the metallic substrate and accordingly shortened the diffusion path before depositing the washcoat. Ferrandon *et al* (1999) developed a technique to grow a number of textured alumina whiskers on the surface of metallic substrate before dip coating, which greatly improved the combination ability between the alumina washcoat and the substrate. Otherwise, the additives, such as rare earth oxides, into washcoat can improve its adhesion on FeCrAl surface (Huang *et al* 2005). Among additives, Ce–Zr solid solutions with good promoted oxygen storage capability (OSC) were widely used in washcoating slurries (Kašpar *et al* 1999; Agrafiotis *et al* 2000; Bedrane *et al* 2002; Nagai *et al* 2002).

In the present work, we mainly study the effect of addition of different amounts of  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution into slurries on washcoat adhesion on FeCrAl foils.

### 2. Experimental

#### 2.1 Materials

Commercially available pure *g*-alumina powders (PURALOX SCFa-140, Sasol Germany GmbH) were used as raw materials in this study, with a specific surface area of 142 m<sup>2</sup>/g. Heat-resistant Cr25Al5Fe alloy foils (0.1 mm thick) were chosen as the metallic substrates.  $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were 99 wt% purity Aldrich products. According to the literature (James and Schwarz 1995; Rossignol *et al* 1999; Bozo *et al* 2001; Trovarelli *et al* 2001; Wu *et al* 2004),  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution was prepared by the method of precipitation with  $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and ammonia.

#### 2.2 Preparation of samples

**2.2a Pretreatment of substrates:** In order to remove oil and superficial impurities, the FeCrAl alloy foils were first ultrasonically cleaned in the solution of detergent and hot water, and then ultrasonically cleaned in alkaline solution and acidic solution. Lastly, the FeCrAl alloy foils were thoroughly rinsed in deionized water. The treated FeCrAl alloy foils were calcined in muffle furnace at 950°C for 10 h, and then were collected for use.

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2.2b *Preparation of coating*: Coating slurries consisting of alumina powders and  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution were prepared with solid content, 30 wt% (table 1). These material powders and deionized water were ball-milled together until 90% granularity of the powder in the batch were  $< 10 \mu\text{m}$ . Then acetic acid was used to adjust pH to 5.5 or so. Then, treated metal foils were covered with slurries by dip coating, and dried at room temperature for 20 min. Subsequently they were dried in an oven at  $120^\circ\text{C}$  for 1 h, and then calcined at  $550^\circ\text{C}$  for 1 h. The above process was repeated until the loading weight was the same as about 10% of metal foils coated.

### 2.3 Measurement of properties

Scanning electron microscopic (SEM) images were taken with JEOL-6300 microscope. SEM was used for the study of morphology of the substrates as well as of the coated foils. The specific surface areas were measured by Brunauer–Emmett–Teller (BET) method from  $\text{N}_2$  adsorption data at  $-196^\circ\text{C}$  with the aid of nitrogen porosimetry (CHEMBET-3000 Instrument). In this paper, the coated specimens cut were so small that they could be put in U-shaped tube for the measurement of BET. The weight used in the calculation of BET was the difference between coated samples and corresponding metal foil. Adhesion of the washcoat upon the metal foil was studied by ultrasonic vibration instrument (120 W, 60 Hz) and thermal shock. The loaded foils were immersed in water medium in an ultrasonic bath for 1 h to measure the weight loss induced by exposure to ultrasonic. Weight loss is calculated by the equation

$$\text{Weight loss} = (w_1 - w_2)/(w_1 - w_3) \times 100\%,$$

where  $w_1$ ,  $w_2$  and  $w_3$  represent the weight of coated foil, after ultrasonic vibration of coated foil and un-coated foil, respectively. The thermal shock test was carried out by exposing the loaded foils in  $1050^\circ\text{C}$  air with SV (space velocity) =  $50,000 \text{ h}^{-1}$  for 1 h, and then taken out to room temperature until cooled to ambience. The above processes were repeated 3 times, and the weight loss measured by ultrasonic vibration.

It is well known that auto-exhaust catalytic support often undergoes high temperature at vehicles acceleration stages. In order to simulate this condition, coating foils were exposed in 10% steam containing air at  $1050^\circ\text{C}$  and with  $\text{SV} = 50,000 \text{ h}^{-1}$  for 10 h or 20 h and then washcoat ad-

hesion and surface area were measured by ultrasonic vibration and nitrogen porosimetry, respectively. Coating foils treated this way are called aged samples; at the same time coating ones untreated are fresh samples.

## 3. Results and discussion

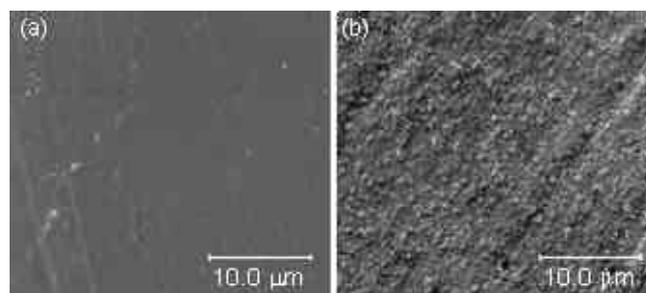
### 3.1 FeCrAl substrate pretreatment at $950^\circ\text{C}$

Before pretreatment, the FeCrAl alloy had a smooth surface (figure 1(a)) which makes the washcoat and catalytic active components difficult to adhere on the metallic substrate. From figure 1(b), we found that the surface of the metallic substrates became more coarse and formed whiskers after high temperature pretreatment, compared to that of untreated one (figure 1(a)). As described in the literature (Tien and Pettit 1972; Molins *et al* 1996; Badini and Laurella 2001), whatever the oxidation treatment temperature, the surface layer contained  $\alpha\text{-Al}_2\text{O}_3$  and non-negligible amounts of Cr and Fe. This is mainly because Al diffuses towards the interface and is oxidated preferentially by oxygen, which may be further demonstrated according to the XRD analysis found in the literature (Wu *et al* 2002, 2005; Zhao *et al* 2003).

Combining with the results of ultrasonic test and thermal shock test of the coated samples (table 2), some conclusions can be drawn that the samples have good coating adhesion after the substrates were pretreated at  $950^\circ\text{C}$  for 10 h.

### 3.2 Adhesion studies of washcoat

Weight loss results of washcoat on FeCrAl foils are shown in table 2. The weight loss discrepancy of the fresh samples with loaded different slurries is smaller according to ultrasonic adhesion test. However, after these samples underwent thermal shock or aging treatment, there were vast differences among weight loss of washcoat with these four slurries. It is evident that the weight loss of washcoat on FeCrAl covered with 1# slurry composing of only  $g\text{-Al}_2\text{O}_3$  is more than that of other three slurries, when thermal shock test and aging treatment were made, viz.  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution can improve the bonding between  $g\text{-Al}_2\text{O}_3$ -



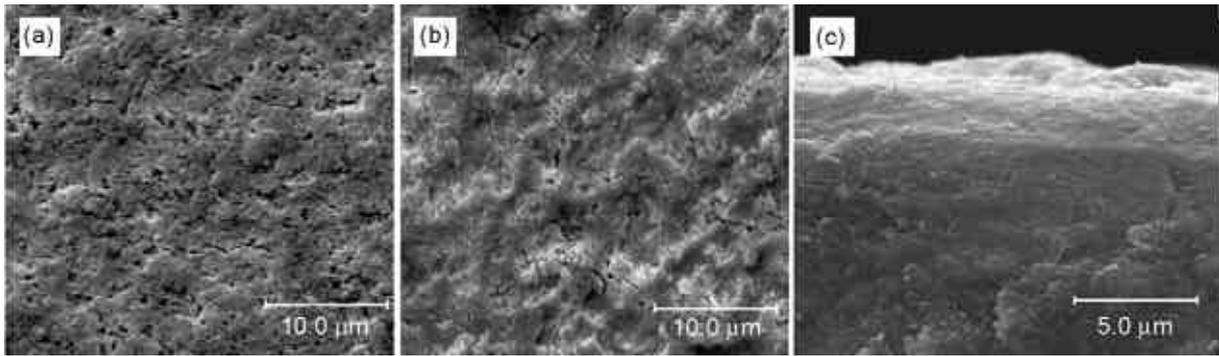
**Figure 1.** Morphologies of metallic foils: (a) untreated and (b) pretreated at  $950^\circ\text{C}$  for 10 h.

**Table 1.** Slurry formulation.

Slurry	Slurry formulation	Solid content
1#	35% $g\text{-Al}_2\text{O}_3$	35%
2#	30% $g\text{-Al}_2\text{O}_3$ +5% $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	35%
3#	28% $g\text{-Al}_2\text{O}_3$ +7% $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	35%
4#	17.5% $g\text{-Al}_2\text{O}_3$ +17.5% $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	35%

**Table 2.** Weight loss results of different washcoats on FeCrAl foils pretreated at 950°C in air for 10 h.

Coated samples	Fresh samples		Aged samples			
	Ultrasonic adhesion test (%)	Thermal shock test (%)	Ultrasonic adhesion test (%)		Thermal shock test (%)	
			Aged 10 h	Aged 20 h	Aged 10 h	Aged 20 h
Coated with slurry 1#	5.04	17.25	27.72	38.13	50.28	65.12
Coated with slurry 2#	1.04	1.26	1.68	2.15	2.26	2.45
Coated with slurry 3#	2.02	2.08	2.57	3.32	3.42	3.90
Coated with slurry 4#	1.81	2.10	2.24	3.31	3.43	3.63

**Figure 2.** Morphologies of coating foils with slurry consisting of 30%  $g\text{-Al}_2\text{O}_3$  + 5%  $Ce_{0.68}Zr_{0.32}O_2$ : (a) fresh coating foil pretreated at 950°C for 10 h; (b) representing (a) sample aged in 10% steam-containing air at 1050°C for 20 h and (c) representing the cross-section of (a) sample.

based coatings and metal foils. We also found that addition of different amounts of  $Ce_{0.68}Zr_{0.32}O_2$  solid solution into slurries play a minor role on weight loss of the washcoat loaded.

As described herein above, we infer that the washcoat loaded slurries containing  $Ce_{0.68}Zr_{0.32}O_2$  solid solution has a good adhesion quality, which can be further demonstrated by SEM micrographs. Figure 2(a) represents the morphologies of the coating surface loaded 2# slurry. From figure 2(a), it is clear that the washcoats on FeCrAl foils pretreated at 950°C are uniformly distributed when slurries contain  $Ce_{0.68}Zr_{0.32}O_2$  solid solution. Additionally, in the SEM micrographs of the cross-section of the coated metal foils (figure 2(c)), the underlayer represents the metal substrate (deep black) and superstratum was the coated layer (grey). It is obvious that no gaps were observed between the metal substrate and the coated layer, which show the good adhesion and integration of the layers. After aging treatment at 1050°C for 20 h, the washcoat (figure 2(b)) had some cracks on the surface of sample to some extent. The SEM micrograph of coating surface loaded 3# and 4# slurry was similar to that of coating surface loaded 2# slurry, so they are not presented in this paper.

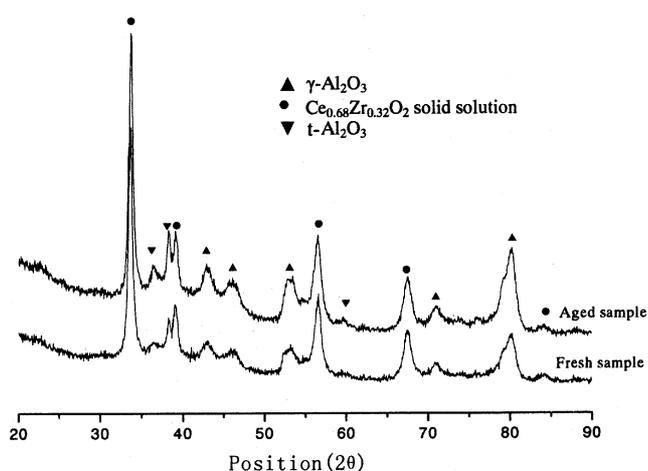
### 3.3 BET surface area analysis

The specific areas are given in table 3, where they are compared between the fresh washcoat and the aged wash-

coat. From table 3, washcoat loaded with the alumina slurry had maximal surface area of different fresh washcoats. This may be explained by the fact that the surface area of the  $g\text{-alumina}$  is bigger than that of  $Ce_{0.68}Zr_{0.32}O_2$  solid solution. A significant decrease of the surface area was observed after aging treatment under conditions of 10% steam-containing air at 1050°C. It can be seen that pure  $g\text{-alumina}$  loses its BET surface area faster than  $Ce_{0.68}Zr_{0.32}O_2$  solid solution especially after ageing for 20 h. The probable reason that caused the above changes is that  $g\text{-alumina}$  has been converted to transient phase of alumina such as  $t\text{-phase}$  due to high temperature (Wu *et al* 2004). This transformation is known to significantly reduce the specific surface area. With the increase of  $Ce_{0.68}Zr_{0.32}O_2$  solid solution proportion in slurries, the BET specific area of washcoat remained still higher when washcoat underwent 20 h ageing process. The thermally stable washcoat is the one derived from the addition of ceria-zirconia solid solution, maintaining about 45 ~ 68  $m^2/g$  of the larger surface area especially when it was calcined for 20 h at 1050°C in 10% steam-containing air. Figure 3 presents XRD patterns of fresh washcoat loaded with slurry containing 30%  $g\text{-Al}_2\text{O}_3$  + 5%  $Ce_{0.68}Zr_{0.32}O_2$  and corresponding aged one exposed in 10% steam-containing air at 1050°C for 20 h. It can be seen clearly that the width of peaks of  $g\text{-Al}_2\text{O}_3$  and  $Ce_{0.68}Zr_{0.32}O_2$  solid solution did not almost increase after coating foil was exposed in 10% steam-

**Table 3.** Specific surface area ( $\text{m}^2/\text{g}$ ) of the various washcoats on FeCrAl foils pretreated at  $950^\circ\text{C}$ .

Washcoats	Specific surface area ( $\text{m}^2/\text{g}$ )		
	Fresh washcoat	Aged washcoat	
		Aged 10 h	Aged 20 h
Washcoat with slurry 1#	128.21	60.86	22.13
Washcoat with slurry 2#	121.57	54.94	45.53
Washcoat with slurry 3#	120.035	60.27	56.30
Washcoat with slurry 4#	108.527	70.40	68.37

**Figure 3.** XRD patterns of fresh washcoat loaded with slurry containing 30%  $g\text{-Al}_2\text{O}_3$  + 5%  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  and corresponding aged one exposed in 10% steam-containing air at  $1050^\circ\text{C}$  for 20 h.

containing air at  $1050^\circ\text{C}$  for 20 h. It can be indicated that crystal particles of  $g\text{-Al}_2\text{O}_3$  and  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution congregated very little at such high temperature. Furthermore,  $t\text{-Al}_2\text{O}_3$  increased negligibly and no other phases of alumina were detected when coating foil was aged at the above conditions. As a result, the addition of Ce–Zr solid solution can improve the thermal stability of  $g\text{-alumina}$  and prevent or delay the alumina transformations, which agrees with the results of open literature (Chen *et al* 2001; Shigapov *et al* 2001; Suhonen *et al* 2001; Wu *et al* 2004).

#### 4. Conclusions

Based on the above analysis, the addition of  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$  solid solution into coating slurries can improve  $g\text{-Al}_2\text{O}_3$ -based washcoat adhesion on FeCrAl foils. Weight loss is below 4.0% even after aging test of 10% steam-containing air at  $1050^\circ\text{C}$  for 20 h. The specific surface area of this washcoat remains at about  $45 \sim 68 \text{ m}^2/\text{g}$  even after aging test at  $1050^\circ\text{C}$  for 20 h, which may be explained by the fact that Ce–Zr solid solution can prevent or delay the alumina transformations. In addition, with the increase of weight

ratio of Ce–Zr solid solution to  $g\text{-Al}_2\text{O}_3$  in coating slurries, specific surface area of washcoat maintain higher via ageing test at  $1050^\circ\text{C}$  for 20 h in 10% steam-air, and there is no linear relation about the effect of the proportion of Ce–Zr solid solution in coating slurries on weight loss of  $g\text{-Al}_2\text{O}_3$ -based washcoat.

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