

Comparison of Sol-Gel Methods for Washcoating Metallic Substrates

F. Akhlaghian¹, J. Towfighi^{1,*}, A. Mohajeri² and A. Zamaniyan²

Abstract. *FeCrAl foils were coated with alumina. Washcoating solutions were prepared using different sol-gel methods. Method A uses an inorganic precursor of aluminum nitrate and a complexing agent of Acetylactone, method B is a hot hydrolysis of aluminum alkoxide, and method C is a modification of method B, by adding aluminum acetylacetonate. The last method, D, is a hydrolysis of aluminum alkoxide at room temperature. Washcoating solutions were deposited on FeCrAl foils through dip coating. Then, the coated foils were dried at 100° C and calcined at 600° C/3 for 2 hours. Ultrasound vibration tests showed a good adhesion of washcoat layers. Characteristics of the washcoat layers were determined by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmet-Teller (BET), and Thermal Gravimetric Analysis (TGA) tests. Results of BET tests show that surface areas in sol-gel methods are greater than those found in the suspension method, and the inorganic sol-gel method (method A) has a lower surface area than those found in organic sol-gel methods.*

Keywords: *Sol-gel; Organic and inorganic precursor; Washcoating; Alumina; Metallic Substrate.*

INTRODUCTION

Nowadays, a considerable amount of attention is being paid to the washcoating of metallic and ceramic substrates. The reason for this phenomenon is due to its use in reactors and structured catalysts. A metallic substrate is preferred due to low weight, high thermal conductivity, ductile capability and high resistance against mechanical vibration and thermal shock [1-4]. A suitable washcoat should have a large surface area, uniform thickness, mechanical stability and good adhesion to metallic substrates [5].

There are many liquid phased based methods for washcoating in literature, some of which are suspension, sol-gel, a hybrid between suspension and sol-gel, and impregnation [3]. Men et al. [6] used a suspension of γ -alumina, deionized water, polyvinylalcohol, and acetic acid. Meille et al. [7] deposited γ -alumina using a suspension method on different microstruc-

tured substances. Stefanescu et al. [8] optimized the suspension preparation parameters of γ -alumina like particle size, viscosity, solid load and binder amount, to reach a good adhesion of the coating film. Germani et al. [9] evaluated the impact of different binders upon suspension methods. Haas-Santo et al. [5] used an organic sol-gel method at room temperature for preparing a thin porous oxide coating to coat the inner walls of a microstructured reactor. Hwang et al. [10] also used an organic sol-gel method based on the hot hydrolysis of aluminum isopropoxide (Yoldas process) for preparing slurry for washcoating a silicon microchannel. Giani et al. [4] used the sol-gel method of pseudoboehmite as a precursor of γ -alumina for washcoating metal foams.

Applying sol-gel methods for washcoating has advantages like high surface area, purity, homogeneity, porosity control, simplicity and the use of cheap equipment [11,12]. Organic sol-gel methods usually use metal alkoxides as a precursor. High prices for industrial use, high reactivity, insolubility in water and most alcohols are the disadvantages of using organic sol-gel methods [13,14].

The aim of this work is to investigate the possibility of applying a low price inorganic precursor (aluminum nitrate) and a comparison of different sol-

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gel methods. It is necessary to mention that the application of foil washcoating is in the manufacturing of metallic micro and monolithic reactors.

EXPERIMENTAL

Pretreatment of Substrates

FeCrAl foils (Fe 72%, Cr 23% and Al 5%) were used as the substrates for alumina washcoatings. The foils were immersed in an ultrasonic bath of a hot solution of detergent and water for cleaning and removing impurities and organic compounds. Then, they were immersed in an ultrasonic bath of alkaline and acidic solutions in turn and in the mentioned order, each immersion lasting for 15 minutes. Finally, the foils were rinsed thoroughly with deionized water.

FeCrAl foils were annealed at 900°C for 10 hours. This thermal pretreatment produces a porous layer of α -Al₂O₃ on the surface of foils [15].

Preparation of the Washcoating Solutions

The following methods were used for the preparation of washcoating solutions:

- A. An aluminum nitrate solution (Merck) was prepared at 1M concentration.

Acetylactone (Merck) was added as a chelating agent. The molar proportion of acetylactone to aluminum nitrate was 3 to 1. The mixture was continuously stirred for 4 days at 80-90°C (method A) [13,14].

- B. Deionized water was heated up to 80-90°C while being stirred constantly.

Aluminum isopropoxide (Merck) was added to water and hydrolyzed. The molar proportion of alkoxide to water was 1 to 100. The solution was stirred at 80-90°C for 1 hour. Nitric acid was added to peptize the alumina sol. The molar ratio of alkoxide to acid was 1 to 0.2. The solution was stirred at 80-90°C for 24 hours (method B) [10,16].

- C. This method was developed by Yoldas [17]. Three grams of aluminum acetyl-acetonate (synthesized through the procedure described below) were added to 50 ml of deionized water. The mixture was heated up to 80-90°C while being stirred constantly. Aluminum isopropoxide (Merck) was added to the mixture and hydrolyzed. The rest of the procedure is entirely similar to method B (method C).

For synthesizing aluminum acetylactonate, 40 ml of deionized water and 8 ml of 5M ammonia were added to a flask containing 3 grams of acetylactone. Then, a solution containing 3 grams of aluminum sulfate hexadecahydrate,

Al₂(SO₄)₃.18H₂O (fluka), dissolved in 30 ml of cold deionized water was prepared.

The solution of deionized water and ammonia was added to the solution of aluminum sulfate and deionized water while being stirred. When the addition of acetylactone solution was complete, the pH of the solution was checked. If the solution was still acidic, 5M ammonia was added drop by drop until it was just basic. Then, the mixture was left at a standstill for 15 minutes before the cream colored product was collected by vacuum filtration. The product was dried in air and then recrystallized in methylene chloride (Merck) [18].

- D. A mixture of aluminum isopropoxide and ethyl alcohol (Merck) was prepared; the molar ratio of aluminum isopropoxide to ethylalcohol being 0.1. Acetylactone was added as a chelating agent with a molar ratio of aluminum isopropoxide to acetylactone of 1.

Hydrolysis was done by adding water with a molar ratio of aluminum isopropoxide to water of 0.5. The pH was adjusted to 4.5 by adding concentrated nitric acid [5,19] (method D).

Deposition of Washcoats

Washcoats were deposited on the foils by using a dip coating technique. The foils were vertically immersed in the washcoating solution for 1 minute. The immersed foils were withdrawn from the washcoating solution at a velocity of 10 cm/min, and vertically drained for another 1 minute. The washcoated foils were dried at 100°C overnight. The samples were heated to 600°C in air with a temperature increasing rate of 3 °C/min, and calcined at this temperature for 2 hours.

Characterization

An ultrasonic technique was used to test the adhesion of the washcoat layer to the FeCrAl foils, and the effects of mechanical stress. The washcoat foils were immersed in a bath of petroleum ether inside a sealed beaker and then left in an ultrasound bath for 30 minutes. Cleaning ultrasonic ASTRA 3D was used for performing these tests.

The degree of crystalline order of the samples was studied by X-ray diffraction at room temperature using a Philips PW 1840 Powder diffractometer at Cu K_α radiation in a diffraction angle range of 2°-90°.

The specific BET surface area of the samples and pore size distribution were obtained using a Micrometrics ASAP 2021 device. Before measuring nitrogen adsorption, the samples were degassed at 300°C for 6 hours.

Morphologic assessment of the washcoated foils and also measurement of the thickness of the washcoat layer were performed using a Philips XL 30, scanning electron microscope (SEM).

Thermal Gravimetric Analysis (TGA) of the washcoating solutions was undertaken in an air atmosphere using a TGA PL device at a heating rate of $10^{\circ}\text{C}/\text{min}$.

The rheological behavior of the prepared washcoating solutions was measured using a rotational stress control rheometer of MCR 300, Physica Anton Paar.

RESULTS AND DISCUSSION

Density and pH

The density and pH of the washcoating solutions have been measured and listed in Table 1. The bouncy method has been used for measuring densities.

Viscosity

For washcoating solutions A, B, C, and D (as shown in Figure 1), when shear rate increases, viscosity also increases slowly which indicates the growth of gel formation.

Thermal Gravimetric Analysis

The thermal behavior of the washcoating solutions was evaluated with TGA tests, and the resulting curves

are shown in Figure 2. The distinct steep slopes of the TGA curves are attributed to the elimination of absorbed water. These parts of the curves terminate at about 25-60 percent of weight and up to around 100°C depending on the sample type. Weight loss continues up to 600°C due to the breakdown of organic materials.

X-Ray Diffraction Studies

XRD patterns of powder samples were recorded in the region of 2° - 90° . Figure 3 shows XRD patterns of samples A, B, C and D. Diffraction patterns of sample A show the formation of amorphous alumina. The XRD reflection of samples B, C and D match with

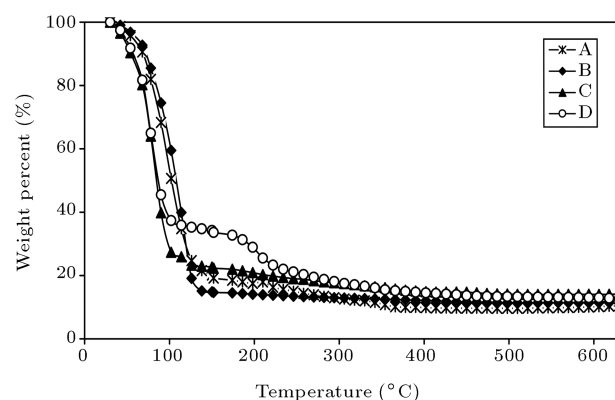


Figure 2. TGA curves for washcoating solutions.

Table 1. Density and pH of washcoating solutions.

Washcoating Solution	Density (ml/g)	pH
A	1.121	0.42
B	1.011	3.98
C	1.013	5.80
D	0.8694	4.50

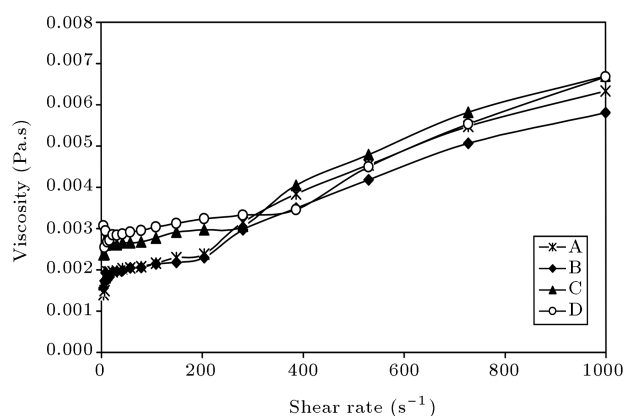


Figure 1. Viscosity versus shear rate for washcoating solutions A, B, C and D.

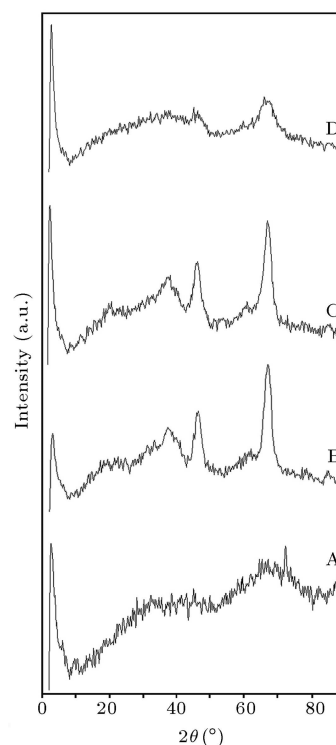


Figure 3. XRD pattern for powder samples.

that reported for the γ -alumina phase (JCPDS files NO. 29-63) with cubic symmetry. The broad peaks of sample D confirm the smaller crystal size of this sample compared to samples B and C (according to the Scherrer equation).

Surface Area and Porosimetry

The specific surface area, pore volume and pore diameter of powder samples have been shown in Table 2. As the results presented in the table show, using inorganic sol-gel methods brings about greater surface areas than the areas reported for suspension methods in the literature [9, 20], but less than the areas reported for organic sol-gel methods. The modified organic sol-gel method (method C) shows the greatest surface area and pore volume.

Figure 4 shows the isotherms of liquid nitrogen adsorption/desorption in different powder samples. The behavior of these isotherms is similar to that of types IV [21]. All samples show hysteresis loops, indicating the presence of mesopores.

A diagram of accumulative volume data from BJH desorption isotherms is shown in Figure 5. The flatness of all cumulative curves at a high pore diameter

Table 2. The specific surface area, average pore volume and average pore diameter of the alumina powder samples.

Powder Sample	Surface Area (m^2g^{-1})	Average Pore Diameter (nm)	Average Pore Volume (cm^3g^{-1})
A	170.1	3.64	0.1564
B	254.2	4.9	0.3112
C	521.4	3.74	0.4870
D	334.0	3.00	0.2498

BET and pore volume are calculated from the BJH adsorption isotherms (average diameter is calculated with $4V/S$. S is considered pore surface area).

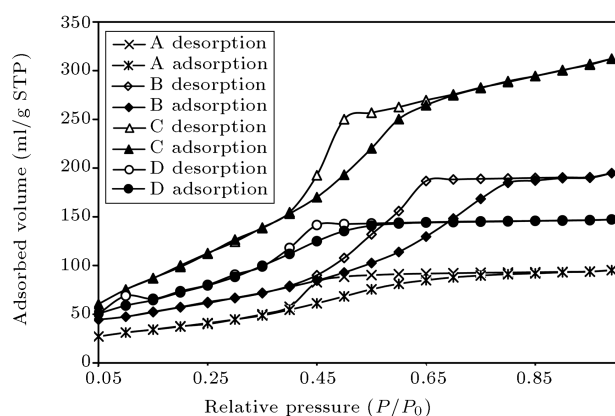


Figure 4. Isotherms of nitrogen adsorption/desorption for powder samples.

region shows that pores with diameters greater than 10 nm can be neglected. Method A yields the lowest accumulative pore volume, and methods B and C have the highest accumulative pore volumes.

BJH pore size distribution curves, which are of the desorption curve data in isotherms, have been shown in Figure 6. For most methods, the diameter of the majority of pores is in the range of 2-10 nm, indicating that all supports are mesoporous. The height of distribution peaks corresponds with pore size in the range of 3 to 6 nm.

Adhesion Tests

The adhesion of the alumina layer to foils was tested using two methods. The first method was a drop test in which the washcoated foils were dropped from a height of 50 centimeters three times and their weight losses measured. No weight loss was observed after each drop.

The second test was adhesion evaluation after ultrasonic vibrations. This ultrasonic test (in a petroleum ether bath) did not show any weight loss either.

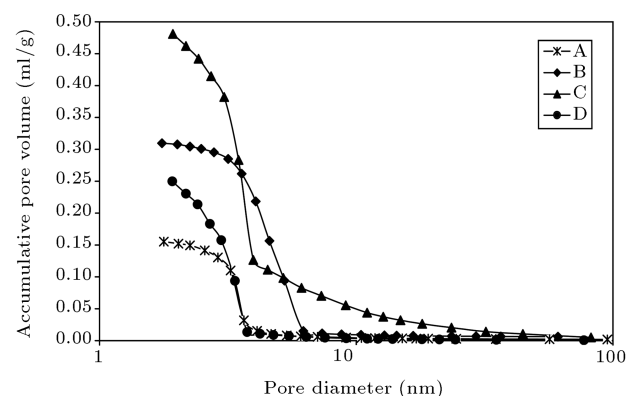


Figure 5. BJH desorption accumulative pore volume versus pore diameter for different powder samples.

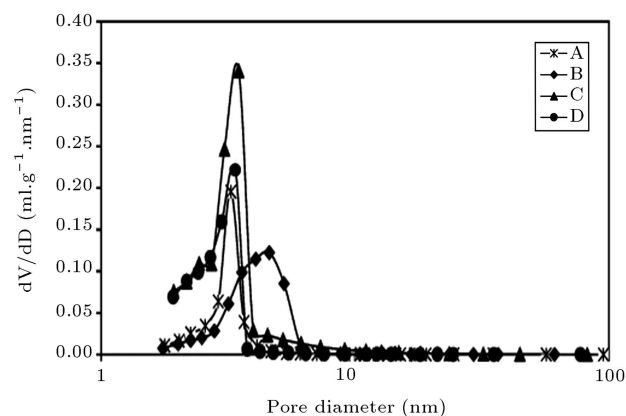


Figure 6. Pore size distribution in accordance with BJH desorption of powder samples.

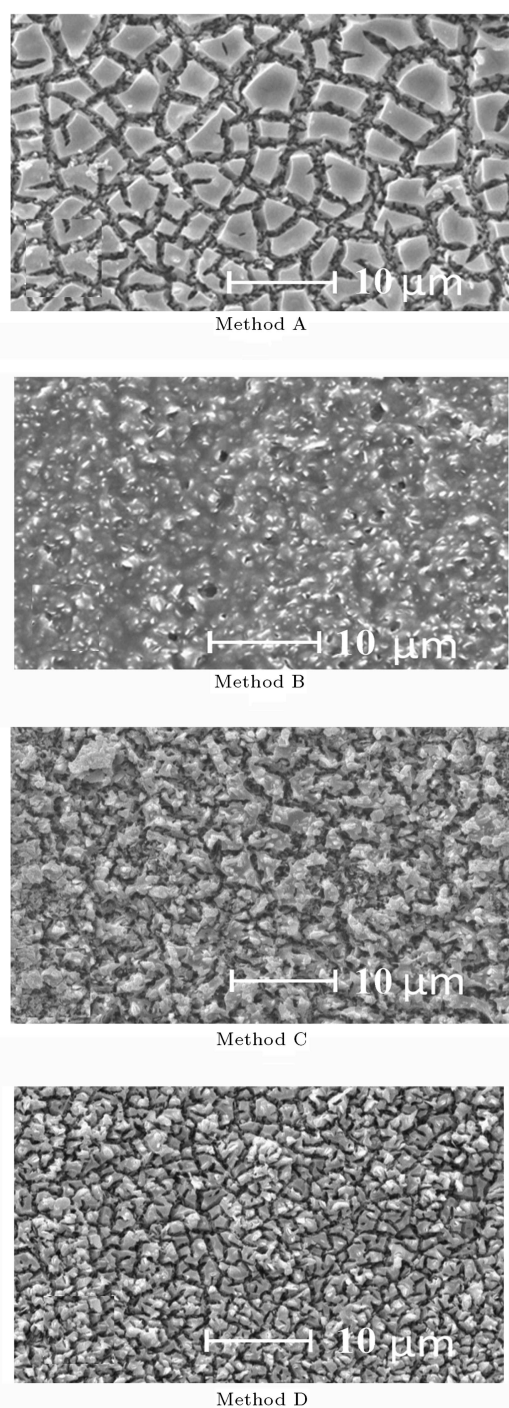


Figure 7. SEM images of alumina washcoat layer on FeCrAl foils.

Scanning Electron Microscopy

The difference in morphologies of the washcoated foils of samples A to D can be seen in Figure 7. Morphologic images have been magnified 2000 times, and show the homogeneous and cracked structures of washcoated foils. The cracks are the result of great differences between the thermal expansion coefficients of the Fe-CrAl alloy and the alumina washcoat layer, and also

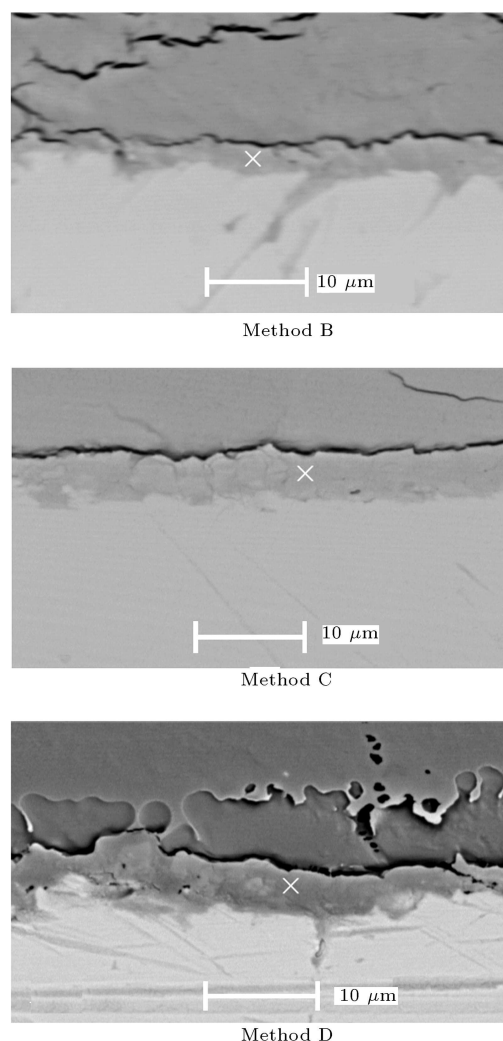


Figure 8. SEM images of cross-sections of FeCrAl foils coated with alumina. Thickness of coating layers in B, C and D methods are 2.93, 4.5 and 4.51 μm , respectively.

the shrinkage of the washcoat layer during the drying and calcination steps. The forms of cracks in samples A, B, C, and D are not the same.

Figure 8 shows SEM images of cross-sections of FeCrAl foils coated with alumina. Adhesion between the alumina washcoat layer and the FeCrAl substrate is very good and the washcoat layer thickness determined by SEM is less than 10 μm .

CONCLUSIONS

For the first time, FeCrAl foils were washcoated using a sol-gel method, which used an inorganic aluminum nitrate. This method of washcoating was compared with methods which use expensive isopropoxide. Ultrasound tests approved the excellent adhesion of coated layers for all methods.

The XRD patterns of alumina samples obtained after calcination show that different alumina struc-

tures can be coated on FeCrAl foils. Surface areas for the sol-gel methods are greater than those of suspension methods. Organic sol-gel methods also come up with higher surface area porosity, compared to inorganic sol-gel methods. SEM pictures show that the morphology of washcoated foil surfaces, using different methods, is different due to their gel formation structure.

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BIOGRAPHIES

Faranak Akhlaghian completed a B.S. course at the Iran University of Science and Technology and a M.S. course at Isfahan University of Technology. At present, she is completing a doctoral degree course in Chemical Engineering at Tarbiat Modares University, in Tehran. The title of her Ph.D. thesis is: 'Monolith and Micro Reactors in Partial Oxidation of Methane'. She serves as a member of the academic board of Kordestan University and has lectured on ten various modules for five years at that university.

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