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Application of plasma spraying in the preparation of metal-supported catalysts

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Abstract

Catalysts supported on metals are widely used today, but room still remains for further improvement of catalyst characteristics. The subject of this paper is the application of a plasma spray for the deposition of alumina coatings on metal substrates of different geometry (plates, foams) for subsequent synthesis of catalysts. The alumina layer sprayed successfully solves two different problems: (i) it serves as a washcoat on which a catalyst is synthesized, and (ii) it protects the metal surface from oxidation at high temperatures. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of new environmentally clean and energy safe technologies is one of today's important tasks. Examples are gas and oil processing, motor fuel production, catalytic removal of VOCs from gas streams and purification of wastewater containing organic compounds. Catalysts to be used in these processes must possess high thermal stability and wear resistance properties.

Application of metal substrates as catalyst supports is becoming more common. Metals have some advantages that make their application in catalysis more attractive than ceramic supports. Their advantages include their high mechanical strength and heat conductivity characteristics. Protection of catalytic coatings against mechanical shock and chemical exposure to the reaction medium and the conservation of the catalytic activity at high temperatures are the main problems when metal-supported catalysts are used. The preparation of materials with strong contact between the catalytic layer and the metal surface at high temperatures is also a very complicated task.

Plasma spray technology offers the possibility of preparing solid surface coatings on metals which will exhibit high mechanical and thermal stabilities. The application of plasma spray methods makes it possible to support both preliminary inert washcoats as well as catalytically active coatings.

Plasma spray of washcoatings of alumina, titania, zirconia, etc., will allow one to solve successfully the problem of adhesion of the active component to the metal surface and to protect the metal-substrates from

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aggressive medium and improve their durability for high temperature use. Moreover, the plasma spray method will give an opportunity to design composite materials consisting of different combinations of plasma-sprayed catalytic and protective layers.

It is important to note that there are no strict limitations on the geometry of granulated or monolithic supports when plasma spray methods are used. Both substrates of simple geometry (flat surfaces) and complex substrates (foam materials and honeycomb monoliths) can be applied successfully.

Although plasma spray techniques are well-developed and in common use today, information on the application of these methods in catalysis is rather scarce. Traditionally, plasma spraying is applied when the formation of dense, non-porous protective layers is necessary and this makes the direct use of this method in catalysis rather complicated.

A number of papers have shown that the porous structure of sprayed coatings depends significantly on the jet outflow regime (laminar, transient or turbulent): the chemical composition and flow rate of the plasma-forming gas, the plasma torch power, the spraying distance, etc. For example, an increase of the plasma-forming gas flow rate and spraying distance leads to a growth of the porosity of the coating and this is accompanied by lower adhesion [1–3]. Changing the particle size of the powder sprayed also allows regulation of the physicochemical characteristics of the layers deposited: the phase composition, the porosity, the specific surface area and the thermal conductivity properties [4,5].

Several publications have been devoted to the application of plasma spraying for the synthesis of catalysts. Two different approaches have been used for the synthesis of catalysts: (i) preliminary spraying of a gradient layer with various additives, followed by deposition of an active component; and (ii) direct spraying of a catalytically active component on a support surface [6–8].

The subject of this paper is the application of direct current (dc) plasma torch [9,10] with the interelectrode insert (IEI) for the atmosphere plasma spraying of the alumina coatings under different regimes of the jet outflow (laminar, transient or turbulent) on the metal substrates of different geometries (plates, foams) for subsequent synthesis of catalysts.

2. Experimental conditions and procedure

Operating modes of plasma torch with IEI (see [9,10]) were provided by the variation of the plasma-forming gas (air) flow rate over a wide range (from 0.5 up to 2.5 g/s); this made it possible to change the velocity of the particles and their aggregate state, and therefore, the coating micro- and macrostructure over the wide range. The main regimes of the plasma torch operation and outflowing jets are presented in Table 1.

The main advantages of the plasma torch used [9,10], as compared with conventional plasma torches are: (i) application of IEI provides a possibility to increase the plasma torch power by increasing the arc voltage (rather than the arc current, as usually); this increasing the continuous operating life of the plasma torch electrodes; (ii) the detected frequency of the arc shunting in plasma torches of this type is one or two orders of magnitude higher in comparison with the large scale shunting (low-frequency) in plasma generators with a self-setting arc length, other conditions being equal; (iii) within a specific range and at equal gas flow rate, pressure, discharge chamber diameter, arc current and other parameters, the mean mass temperature of the gas at the outlet of the output electrode of a plasma torch with IEI is always higher than in a plasma generator with a self-setting arc mean length; this is explained by a higher electric field of the turbulent arc and by a possibility of varying the IEI length; (iv) realization of a ‘‘diffusive’’ arc attachment on the anode surface provides an axial symmetry of the exhausting plasma flow, this increasing the stability and reproducibility of the parameters of the high-temperature flow in the repeated torch activation; (v) the use of air as a working gas, when there are no strict requirements to the gas composition, reduces substantially the cost of plasma technologies and speeds up the equipment pay-back and (vi) the use of the plasma torch operating mode with a quasi-laminar jet outflow makes possible new effective technologies of powder (primarily oxide) materials and surface treatment.

The principal scheme of the powder plasma spraying set-up, used in this work, is presented in Fig. 1. Alumina powders differing in phase composition and particle size (α-Al_2O_3 20–80 and γ-Al_2O_3 90–500 μm) were used to spray a washcoating layer on titanium plates and nickel foam materials. The active phase was

Table 1
Main regimes of the plasma torch operating and outflowing jets

Flow rate of plasma-forming gas (air) G_g (g s^{-1})	0.5	0.75	1.0	1.25	2.0	2.5
Arc current I (A)	255	250	245	240	220	210
Arc voltage U (V)	180	200	210	220	250	270
Efficiency of electric energy utilization η (%)	45	50	60	65	70	72.5
Effective thermal power of outflowing plasma jet (kW)	20.6	25.0	30.8	34.3	38.5	41.1
Regime of the plasma jet outflow and approximate length of powder thermal treatment zone in axial direction, L_r (m)	Laminar	Laminar–transient	Transient	Transient	Turbulent	Turbulent
	0.15	0.09	0.075	0.06	0.05	0.05
Mean-mass temperature of plasma prior to powder injection section/K	8450	7600	7400	7150	6400	6150
Mean-mass velocity of plasma prior to powder injection section (m s^{-1})	460	570	720	815	1020	1160
Characteristic times of heating (ms) corresponding to particles of different size (mkm)						
20	0.96	0.6	0.46	0.35	0.24	0.22
40	1.5	0.96	0.71	0.55	0.38	0.33
70	2.1	1.3	1.0	0.77	0.54	0.49
90	2.4	1.6	1.1	0.89	0.65	0.58
200	3.9	2.5	1.9	1.5	1.1	0.99
300	5.3	3.4	2.6	2.0	1.5	1.3
400	6.5	4.1	3.1	2.5	1.8	1.6
500	7.6	4.8	3.6	2.9	2.1	1.8

synthesized by impregnation of the plasma sprayed layer with lanthanum and cobalt cations. In some cases, the modification of the plasma-sprayed layer was provided by the deposition of lanthanum-containing γ-Al_2O_3 to increase the specific surface area of the washcoating layer. For comparison, the same catalysts on Ni foam supports were synthesized using the technique described in reference [11], which includes a direct synthesis of a γ-Al_2O_3-containing washcoat on the metal surface by a chemical method without the formation of plasma-sprayed layer.

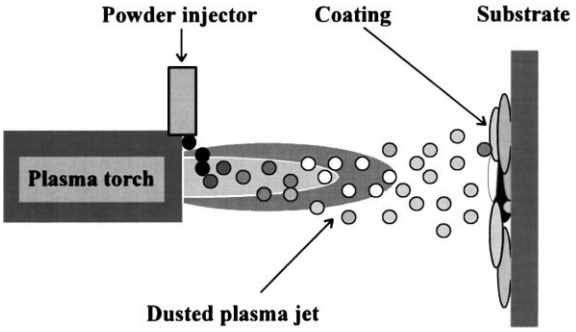

Fig. 1. Schematic diagram of the plasma spray set-up.

X-ray analysis of the samples was carried out using a HZG-4 diffractometer with copper radiation in the 2θ range of 20–55°. To specify the parameters of the solid solutions and of the perovskite composition, the data were obtained in the range of 2θ of 62–72°. The specific surface areas of the samples were measured by the BET method and the pore volumes of the sprayed layers were calculated using the water capacity technique. The morphology of the catalysts was characterized by SEM. The catalytic activity was

Table 2
Properties of γ-Al_2O_3 after plasma treatment and cooling in water

Particle size (μm)	Flow rate (g s^{-1})	Regime	Specific surface area (m^2 g^{-1})	Phase composition	I_α/I_γ[a]
90–200	0.5	Laminar	2.2	α-Al_2O_3, γ-Al_2O_3	30
90–200	1.0	Transient	22	α-Al_2O_3, γ-Al_2O_3	13
200–300	0.5	Laminar	19	α-Al_2O_3, γ-Al_2O_3	25
200–300	1.0	Transient	76	α-Al_2O_3, γ-Al_2O_3	11
300–400	0.5	Laminar	67	α-Al_2O_3, γ-Al_2O_3	8
300–400	1.0	Transient	104	α-Al_2O_3, γ-Al_2O_3	6
400–500	0.5	Laminar	119	α-Al_2O_3, γ-Al_2O_3	

[a] I_α/I_γ ratio of intensities of line d/n=2.085 (α-Al_2O_3) and d/n=1.990 (γ-Al_2O_3).

tested for the methane oxidation reaction in a flow set-up; the reaction mixture was 1% CH_4 in air with a volume velocity of 400 h^{-1}.

3. Result and discussion

As mentioned before, the jet outflow regime and powder particle size define physicochemical characteristics of coatings sprayed. A preliminary study of the influence of the plasma regimes on the properties of alumina powders plasma treated and cooled in water has been performed. The results for γ-Al_2O_3 powder are presented in Table 2.

A comparison of cross-section views of initial and plasma-treated and cooled in water particles of γ-Al_2O_3 showed that in the latter case the pellet consists of a core and a shell (Fig. 2). The densities of these two basic areas are different. A comparison of the scanning electron micrographs of the initial and the plasma-treated and cooled in water particles and the analysis of XRD data allow us to suggest that the particle core consists of γ-Al_2O_3 phase, while the particle shell is made of α-Al_2O_3. It seems that the use of large particles for spraying and high cooling velocities leads to the formation of a cool core and a hot melted shell. This conclusion was confirmed by the numerical modeling of the temperature distributions inside the particles of γ-Al_2O_3. The method used is described in reference [10]; it took into account the temperature gradient under heating and complicated aggregate state of the particle.

At the same time, experiments on the plasma spraying of alumina of different phase composition and particle size on titanium plates showed that the properties of plasma sprayed layers are quite similar and do not depend significantly on the jet outflow regime used (Table 3).

When α-Al_2O_3 was sprayed on titanium plates, the coatings were characterized by a low specific surface area; meanwhile, their pore volume increased when the spraying regime was changed from laminar to turbulent.

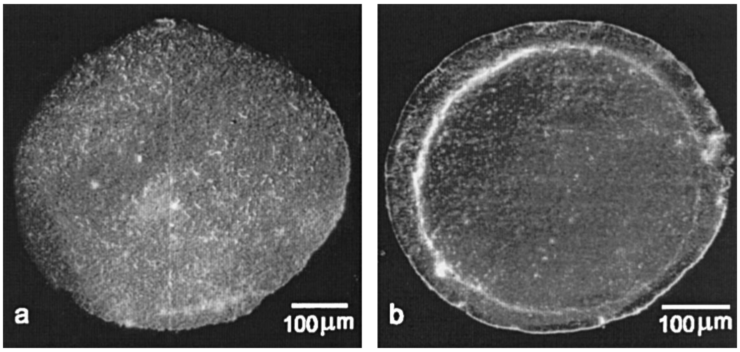

Fig. 2. Micrograph of a cross-section view of (a) initial and (b) plasma-treated γ-Al_2O_3 particles.

Table 3
Properties of alumina sprayed on titanium plates

Particle size (μm)	Type of alumina sprayed	Flow rate (g s^{-1})	Regime of plasma jet outflow	Specific surface area (m^2g^{-1})	Phase composition	Pore volume (cm^3 g^{-1})
40	α-Al_2O_3	0.75	Laminar–transient	0.2	α-Al_2O_3	0.052
40	α-Al_2O_3	1.25	Transient	0.2	α-Al_2O_3	0.065
40	α-Al_2O_3	1.75	Turbulent	0.2	α-Al_2O_3	0.167
90–200	γ-Al_2O_3	0.5	Laminar	0.2	α,θ-Al_2O_3	0.068
90–200	γ-Al_2O_3	0.75	Laminar–transient	0.4	α,θ-Al_2O_3	0.075
90–200	γ-Al_2O_3	1.0	Transient	0.6	α,θ-Al_2O_3	0.166

It was established that the dependence of the regime on the coating properties was the same when γ-Al_2O_3 was sprayed. Moreover, in the latter case, the spraying regime influenced the quantitative proportions of the α-Al_2O_3 and θ-Al_2O_3 phases of the coatings and their specific surface areas. The maximum pore porosity and minimum α-Al_2O_3 phase content were registered when a transient jet outflow regime was used.

The disagreement in the data for the phase compositions and the specific surface area for γ-Al_2O_3 powders plasma treated and cooled in water and for γ-Al_2O_3 sprayed on Ti plates may be explained by significant differences in the quenching rate in the experiments performed. The formation of dense layers when γ-Al_2O_3 was sprayed on titanium plates was confirmed by scanning electron microscopy (Fig. 3). It is obvious that the contact between the alumina and the metal surface was rather strong and uniform. The sprayed layer had a complicated structure, consisting of dense areas and macropores of different forms and sizes.

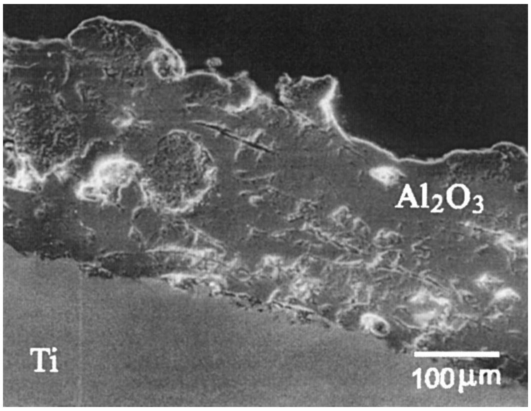

Fig. 3. Micrograph of a cross-section view of γ-Al_2O_3 plasma-sprayed on Ti.

The direct deposition of the active La–Co component on these supports leads to the formation of $LaCoO_3$ and Co_3O_4 phases, as shown by XRD. The quantities of the supported active component did not exceed 2 wt% because of the low porosity of the sprayed alumina layer. A modification of the sprayed layer by La-containing γ-Al_2O_3 allowed an increase of this value by one order of magnitude. The phase composition of the modified catalyst after the deposition of the active La–Co component was more complex. Besides the presence of the $LaCoO_3$ and Co_3O_4 phases, $LaAlO_3$ perovskite was also formed.

The procedure described was applied to the synthesis of catalysts on Ni foam supports. The external surface of α-Al_2O_3 sprayed on the metal foam support had a complex structure; there were a number of splats differing in appearance and thickness (Fig. 4). The modification of the plasma-sprayed alumina coating by La-containing γ-Al_2O_3 leads to the formation of a top layer on the plasma sprayed alumina (Figs. 5 and Fig. 6). SEM showed also the presence of an intermediate region sprayed between a top layer consisting of γ-Al_2O_3 and dense plasma sprayed α-Al_2O_3 coating. This layer is probably formed at the end of the spraying process (the "switching off" moment) when a moderate temperature regime is realized, this leading to the formation of a layer with higher porosity than the basic one.

The SEM study of catalysts supported on Ni foams coated by plasma-sprayed alumina and modified by La-containing γ-Al_2O_3 revealed that the La–Co component was concentrated in the modifying layer (Fig. 6). XRD showed the formation after calcination at 1000°C of the main $LaAlO_3$ phase and a solid solution based on γ-Al_2O_3.

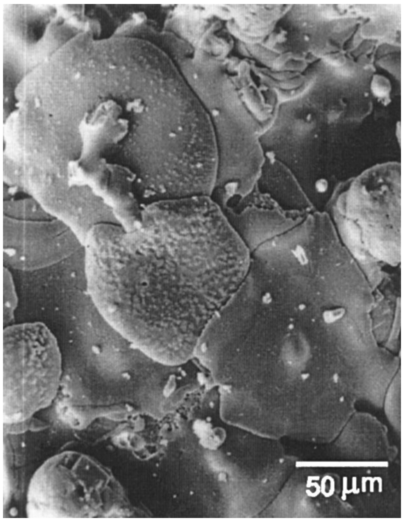

Fig. 4. Micrograph of plasma-sprayed alumina on a Ni foam support.

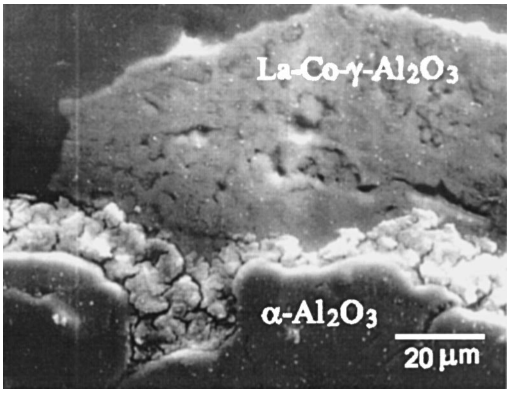

Fig. 6. Micrograph of a cross-section view of a catalyst consisting of La–Co on a Ni foam support.

Changes of the characteristics of the samples following various temperature treatments were examined by XRD and BET measurements and their activities for the methane oxidation reaction were also determined. An increase of the calcination temperature from 600°C to 1000°C caused a decrease in the BET area of the samples from 20 to 8 m^2/g, while the temperature to give 50% methane conversion increasing from 460°C to 610°C.

The properties of the catalysts developed were compared with those of catalysts having the same phase composition and BET surface area but synthesized without the use of a plasma-sprayed alumina layer. The catalysts calcined at temperatures from 600°C to 1000°C demonstrated the same level of activity as catalysts synthesized using the plasma technique. A difference in the activity between these types of catalysts appeared when the duration of calcination at 1000°C was increased from 3 to 9 h. There was no decrease in the activity of the catalyst with a plasma-sprayed alumina layer whereas the temperature to give 50% conversion rose from 600°C to 655°C for the catalyst prepared without a plasma-sprayed layer (Fig. 7). It appeared that a plasma-sprayed washcoating layer consisting of alumina on a Ni foam support prevented the nickel from

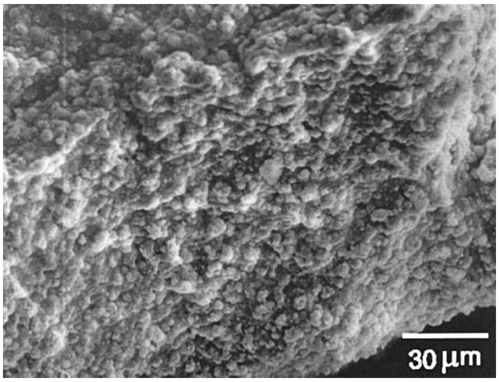

Fig. 5. Micrograph of a modifying γ-Al_2O_3 layer supported on a plasma-sprayed alumina.

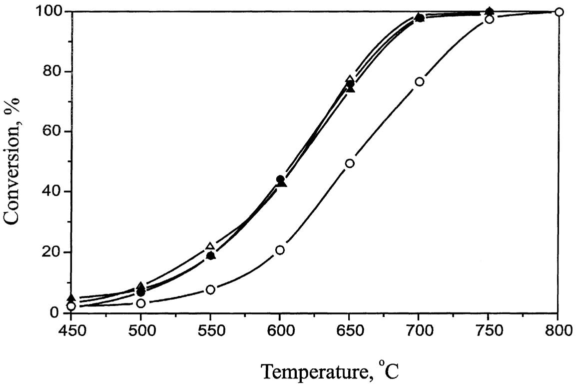

Fig. 7. Temperature dependencies of methane conversion (1% CH_4 in air) on catalysts: (▲) La–Co/Ni, plasm., T_{calc}=1000°C for 3 h; (△) La–Co/Ni, T_{calc}=1000°C for 3 h; (●) La–Co/Ni, plasm., T_{calc}=1000°C for 9 h; (○) La–Co/Ni, T_{calc}=1000°C for 9 h.

becoming oxidized more successfully and increased the thermal stability of the catalyst.

4. Conclusion

In this paper we have presented our first results of a comprehensive study of catalysts prepared on metal supports for high temperature combustion developed using plasma spray methods. Undoubtedly, application of the plasma spray technology in this area is very promising. Experiments performed on metal supports of different geometry have shown that a sprayed alumina layer has a strong and uniform adhesion to the metal surface. The gradient layer sprayed successfully solves two different problems: (i) it serves as a washcoat on which a catalyst can subsequently be synthesized; and (ii) it protects the metal surface from oxidation at high temperatures.

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References

[1] T. Yoshida, Appl. Chem. 66 (1994) 1223.
[2] J. Ilavsky, J. Forman, P. Chraska, J. Mater. Sci. Lett. 11 (1992) 573.
[3] S. Uematsu, T. Senda, Proceedings of the Eighth International Symposium on Plasma Chemistry, vol. 4, Tokyo, 31 August–4 September 1987, p. 1958.
[4] D.J. Varacalle, Proceedings of the Third Material Resources Society Symposium, Reno, 5–9 April 1988, Pittsburgh, p. 541.
[5] Ke-Shun Shi, Z-Y. Qian, M-S. Zhuang, J. Am. Ceram. Soc. 71 (1988) 924.
[6] J.V. Gorynin, B.V. Farmakovskii, A.P. Khinsky, Patent USA, no. 5 204 302 (1991).
[7] H.R. Khan, H. Frey, J. Alloy. Compounds 190 (1993) 209.
[8] S.V. Dozmorov, A.N. Pestryakov, SU Patent no. 1 695 978 (1989).
[9] V.I. Kuz’min, O.P. Solonenko, M.F. Zhukov, Proceedings of the Fourteenth International Thermal Spray Conference, 25–28 May 1995, Kobe, Japan, p. 1091.
[10] O.P. Solonenko, in: O.P. Solonenko, M.F. Zhukov (Eds.), Thermal Plasma and New Materials Technology. Vol. 2. Investigation and Design of Thermal Plasma Technologies, vol. 7, Cambridge/Interscience, UK, 1995, p. 97.
[11] O.Yu. Podyacheva, A.A. Ketov, Z.R. Ismagilov, V.A. Ushakov, A. Bos, H.J. Veringa, React. Kinet. Catal. Lett. 60 (1997) 243.