THE SYNTHESIS OF FINE PARTICLES DURING PLASMA SPRAY PYROLYSIS PROCESS

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Present study offers the technology for production of small uniform particles and coatings by employment of nonequilibrium plasma at atmospheric pressure. A new process has been developed for a high rate plasma deposition of fine particles from solid carbon, aluminum hydroxide and some other related precursor powder. The SEM micrographs showed the features of synthetized carbon particles injected into plasma jet reactor before and after plasma treatment. Shape and size of these particles strongly depend on the localization of inserting place. Significant differences in size and shape were observed over deposition process when initial carbon powders were feeding directly into the reacting arc zone together with propane-butane gas. The carbon film elements deposited on a quartz substrate with addition of propane-butane showed the minimal size and streamline shape. Visual and SEM observations confirmed that carbon coatings proved to be suitable for further deposition of catalytic and tribological coatings.

PACS: 52.40.Hf, 81.15.Rs

INTRODUCTION

Plasma-assisted deposition of wide range coatings and plasma-assisted processing of sprayed substances have become key processes in many scale of application. It is well known that thermal spray pyrolysis may affect the formation of fine particles or granules [1]. The similar process may occur also during plasma spraying. It follows that the dominant process of composition changes during plasma spraying may be spray pyrolysis. Therefore we proposed to perform a series of experimental and theoretical investigations to test the effect of injection of non-reacting and reacting gas mixture such as propane-butane into plasma jet reactor or plasma torch anode. This allowed the presence of higher temperature inside the reactor.

The employment of plasma spray pyrolysis may be directed at the fabrication of variety of ceramic coatings, production of fine mineral fibre and granules, synthesis of micro- and nanostructured particles and plasma polymer products [2,3].

EXPERIMENTAL EQUIPMENT AND TECHNICAL DETAILS

Fine particles were deposited employing a specific plasma spray technique with a linear, sectional plasma torch (Fig. 1) generating non-equilibrium plasma jet at atmospheric pressure. The similar plasma spray torch 100 kW of power is analyzed in details elsewhere in [4]. Plasma chemical reactor which is directly connected to the plasma torch anode 9 consists of two sections 0.02 m of length produced of high purity copper and cooled by water. The internal diameter of the reactor is 0.01 m and total length is 0.04 meter. Such design enables easy to change the length and configuration of the reactor, as well as the flow direction and the exposure duration of material processed.

Experiments were performed at plasma flow temperature 2500 – 3500 K and velocity 300 – 450 $m \cdot s^{-1}$ The diameter of particles was evaluated from the cross-sectional scanning electron microscopy (SEM) observation and the surface zone phase composition was analyzed by X-ray diffractometer.

Coatings and particles were deposited without intermediate layers. Instantly, dispersed particles or thick films of fine structure were obtained during plasma spraying process when raw stuff were introduced into three places of the plasma equipment. Firstly, fine particles and coatings were formed in the nitrogen plasma at atmospheric pressure when initial powder was injected into plasma jet in the outside area of exhaust nozzle of plasma generator perpendicular to plasma jet.

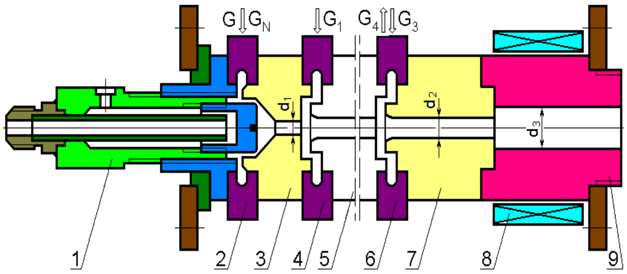

Fig.1. The schematic presentation of plasma torch: 1 – cathode junction, 2,4 – rings of injection of plasma forming gas, 3 – intermediate anode, 5 – neutrode, 6 – powder injection ring, 7,9 – anode, 8 – magnetic coil

The second way of injection is related to the increasing temperature, kinetic energy of powder and their exposure time in high temperature zone. In this case precursor powder was injected into nitrogen plasma flow inside the reactor. The third place of powder injection was reacting arc zone when precursor powder was injected directly into the arc together with additional gas. Instead of previously used two rings for injection of plasma forming gases (Fig. 1.) the third one has been arranged (G_3). Plasma forming gas was supplied via the first ring (G_1), the propane-butane gas via second (G_2). Therefore the length of plasma torch has increased. Coatings were deposited on the surfaces of different kind of substratum, such as stainless steel, silicon, quartz glass or ceramics

RESULTS AND DISCUSSION

A new process is going to be developed for a high rate plasma deposition of solid films and particles from solid carbon monomer precursor (Fig. 2.). Dispersed powder particles (in the present case – carbon and its mixtures with Al $(OH)_3$) injected into the plasma assume the portion of the kinetic and potential energy from plasma flow. In motion together with plasma they became motile rapidly and their edges were melted and shaped.

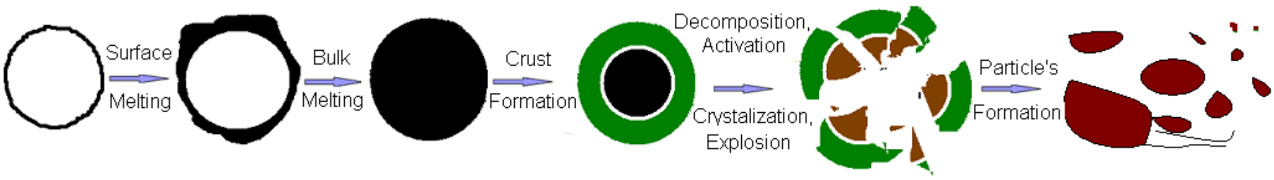

Fig. 2. Model formation of fine particles during plasma spray pyrolysis

Passing the way from plasma torch exhaust nozzle to the substratum or selecting device particles leaves the distance equal 90 – 120 mm. Injected into flow almost all particles leaves the distance being as partly melted.

Fine particles of carbon have been produced by plasma processing of irregularly shaped initial powders. In the case when additional propane-butane gas is not supplied the size and shape of final product depend on the injection location of the initial stuff. As is visible from Fig. 3a and b only several groups of particles has changed their shape and size. The view is different when powder is supplied into diffuse arc column. The shape of particles are not particularly uniform although a smaller particles are better formed (Fig. 3c). At the same arc current the plasma forming gas flow rate may have only negligible impact on size and shape distribution of grains.

During the initial phase of plasma spraying process when powder particles are injected into the reactor or into the arc zone, in the reason of the affect of high temperature flow they may be completely melted and partly evaporated. This occurs when the particle size is relatively small and the velocity of the plasma flow is relatively low at the temperature of 3200 – 3500 K. In the middle of distance between exhaust nozzle and substratum the shape of particles is substantially uniform.

Significant differences in size and shape were observed during plasma spray deposition process when carbon particles were stocked directly into the arc together with propane-butane gas. These particles were selected and separated in the specific filter made. Carbon particles deposited on a quartz and silicon substrate with addition of propane-butane gases has minimal size and streamlines shape (Fig. 4) because of partial evaporation, explosion and secondary formation of the new fine particles during the plasma spray pyrolysis process. The ratio of fine down of the treated powders increases with the increase of propane-butane flow rate in plasma. The diameter of such particles is in general in the range between 2 µm and 50 nm.

Intensive cooling the substratum surface the substance vapour should condense and form a film on the surface significant thinner as in the case of conventional plasma spraying. However this didn‘t occur although the dimensions of elements of coatings were rather smaller, i.e. reached up to 5 – 10 µm instead of 50 µm.

When dispersed particles are injected directly into the arc and the spray distance is decreased the significant changes on the surface of coating were not observed although increasing SEM magnification until 2000 times some increase of coating elements was noticed.

Films of fine particles were formed on a quartz glass substratum intensively cooling it. Proper conditions to the formation of carbon containing coatings are achieved when exhaust temperature in plasma torch exhaust nozzle reached 3200 K and the flow velocity – 320 $m \cdot s^{-1}$. The diameter of elements of such coating didn‘t exceed 2 µm.

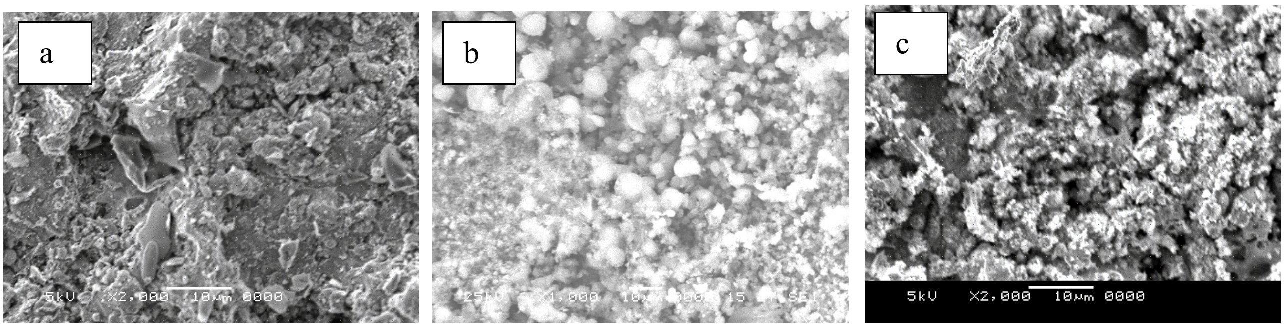

Fig. 3. SEM image of particles produced of 50% C and 50% $Al(OH)_3$ mixture at different injection location of initial powder: a – into plasma jet outside the reactor; b – into the reactor; c – into the arc column

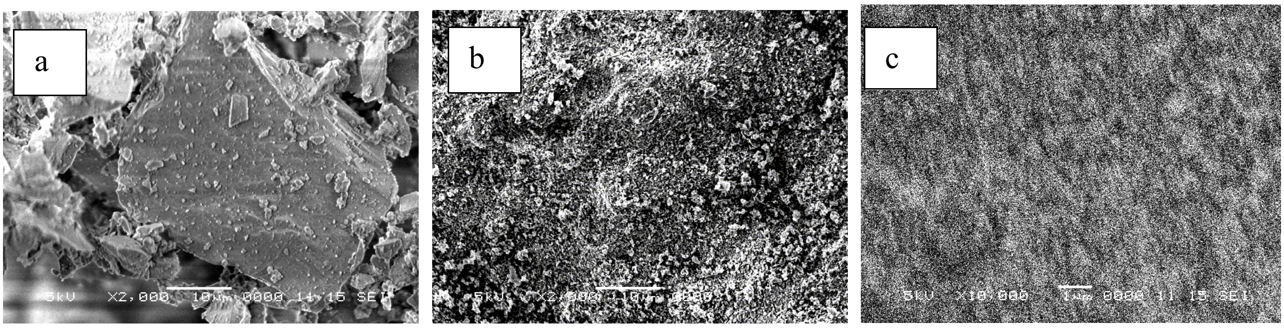

Fig. 4. SEM topography of carbon particles selected on quartz glass surface. Initial powder injected into arc reacting zone together with propane-butane gas. a – initial powder, b – injected into the reactor; c – injected into the arc

At the fairly high arc current the plasma jet temperature may reach the value at which plasma spray pyrolysis occur and prism shaped particles fed into plasma jet reactor may shape as hollow spheres [3]. The size of such granules strongly depends again on injection location of initial substance and time of duration in high temperature zone. The spherical granules obtained by the plasma spray pyrolysis 50 – 100 μm of diameter consist of unagglomerated and uniform octagonal elements with mean length of edge between 40 and 50 μm, which is equal to the mean diameter of original initial particle [3]. Under certain processing conditions Al_2O_3 powders have been completely spheroidized. The morphology and structure of individual particles were examined and their formation mechanism was discussed elsewhere in [3].

It is important to notice that employing the presented method is possible to obtain nanosized particles and nanostructured coatings. Obtained particles are mainly spherical, their sizes vary from 20 to 300 nm.

CONCLUSIONS

Realization of plasma spray pyrolysis process enables the synthesis of well shaped micro- and nanostructured particles and coatings.

The structure of deposited coatings, shape and size of dispersed particles depend on the inlet location of initial substance and means of plasma processing. By injecting particles directly into the reacting arc zone fine-grained structures have been available.

Injecting carbon particles up to 50 μm in diameter into reacting arc zone and blowing additionally propane-butane gas it is possible to obtain coatings diameter composing elements of which doesn't exceed 2 μm.

ACKNOWLEDGEMENT

This work was partly supported by Lithuanian State Science and Studies Foundation and Agency for International Science and Technology Development Programs in Lithuania.

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Article received 22.09.08.

СИНТЕЗ МЕЛКИХ ЧАСТИЦ В ПРОЦЕССЕ ПИРОЛИЗА ПЛАЗМЕННОГО РАСПЫЛЕНИЯ

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Представлена технология пульверизации мелких частиц с помощью неравновесной плазменной струи при атмосферном давлении. Метод плазменного пиролиза распылением разработан с целью получения мелких гладких микрочастиц из порошка углерода, гидрокиси алюминия, доломита, песка и некоторых других материалов. Исследования сканирующим электронным микроскопом (SEM) показали разницу между дисперсными частицами, вдуваемыми в плазменный струйный реактор, и частицами, полученными после обработки в плазме. Получено, что диаметр и форма частиц резко зависит от локализации введения их в плазменный поток. Существенные изменения величины и формы замечены во время плазменного напыления, когда порошки углерода совместно с несущим газом подавались прямо на реактивную зону дуги плазмотрона. При насаждении покрытий углерода на подложку из кварцевого стекла, вместе с порошком сырья, подставляя смесь пропана-бутана, получена мелкозернистая пленка с элементами минимальных размеров и блестящей формы. Оптическая микроскопия и SEM исследования образцов подтверждает пригодность метода при нанесении каталитических и трибологических покрытий.

СИНТЕЗ ДРІБНИХ ЧАСТОК У ПРОЦЕСІ ПІРОЛІЗУ ПЛАЗМОВОГО РОЗПИЛЕННЯ

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Представлено технологію пульверизації дрібних часток за допомогою нерівновагого плазмового струменя при атмосферному тиску. Метод плазмового піролізу розпиленням розроблений з метою одержання дрібних гладких мікрочастинок з порошку вуглецю, гідрокису алюмінію, доломіту, піску і деяких інших матеріалів. Дослідження скануючим електронним мікроскопом (SEM) показали різницю між дисперсними частками, які вдуваються в плазмовий струминний реактор, і частками, отриманими після обробки в плазмі. Отримано, що діаметр і форма часток різко залежить від локалізації введення їх у плазмовий потік. Істотні зміни величини і форми замічені під час плазмового напилювання, коли порошки вуглецю разом з несучим газом подавалися прямо на реактивну зону дуги плазмотрона. При насадженні покриттів вуглецю на підкладку з кварцового скла, разом з порошком сировини, підставляючи суміш пропану-бутану, отримана дрібнозерниста плівка з елементами мінімальних розмірів і блискучої форми. Оптична мікроскопія і SEM дослідження зразків підтверджує придатність методу при нанесенні каталітичних і трибологічних покриттів.