

PLASMACHEMICAL OBTAINING OF HOLLOW SPHERICAL OXIDE PARTICLES SUITABLE FOR THERMAL SPRAYING

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The field of powder applications depends to a considerable extent on the shape and surface of individual particles. In paper [1] the results of electronic-microscope studying of the morphology of particles produced by plasma decomposition of solutions of inorganic salts were submitted. Unfortunately in that paper the numbering of figures and their captions were mixed up on printing. In Fig. 1, the pictures of particles CeO_2 from nitrate solution and ZrO_2 from sulfate solution are represented for example.

A lot of interesting information about the formation of particles with a different morphology using a variety of spray pyrolysis techniques can be found in the review [2]. The reviewed material [2] shows that the spray pyrolysis techniques allow to produce dense (solid), hollow, porous, or fibrous particles and even to deposit thin films, but the formation of hollow spherical particles is the most typical. The authors of this review point to the fact that they do not know anyone who has taken advantage of the possibility for controlled hollow particle synthesis. Theoretical estimations conducted in [3] show that the main advantage of using spherical hollow particles for thermal spraying is the possibility to use coarser powders.

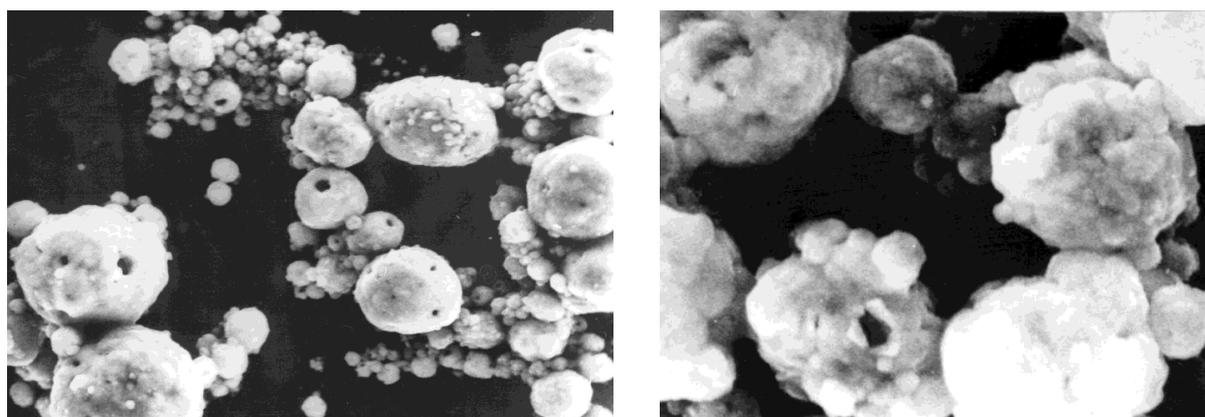


Fig. 1. Pictures of particles CeO_2 from nitrate solution and ZrO_2 from sulfate solution

In the present paper the results of the above works are considered from the point of view of the possibility and expediency of using plasma spray pyrolysis for production of powders for thermal spraying. Also some new experimental data are described and the problem of

anion impurity which is common for plasma pyrolysis is discussed in connection with the impurity influence on the thermal spraying technology.

In Fig. 2 [1] the scheme of a microwave plasma chemical plant used for spray pyrolysis of solutions is demonstrated. The solutions were sprayed by pneumatic sprayer 3 into a low speed (~ 1 m/s) flow of plasma generated by using MW plasma generator 1 (MW power ≤ 5 kW). The process of spraying could be observed through the window 2. The temperature T of the process was controlled in the lower part of thermal isolated reactor 4. Powders accumulated on the inner surface of the reactor, in bunker 6 and mostly on the net metal filter 5. The separated gaseous products were partially condensed in heat exchanger 7 and trickled down to receptacle 8.

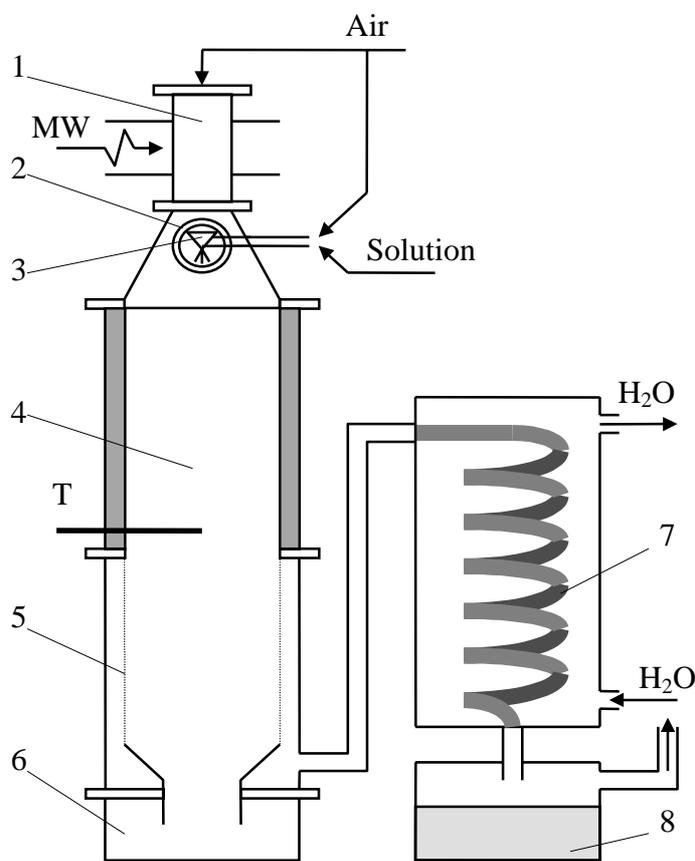


Fig. 2. Scheme of microwave plasma chemical plant

With the help of this plant the powders were produced. According to [1] the formation of a spherical solid shell after the stage of solution drop drying is typical for the cases when the solid residue is nonvolatile and not fusible. Further transformations of the spherical shell formed is determined by the heating rate. If the heating rate is high and if the inner gas emanation is high too the spherical shells are destroyed. If the heating rate is low the particle dries up slower, the size of the spherical shell appears less than the size of a drop, and the shell can remain intact and rather strong.

In [1] it is noted that the formation of small (~ 1 μm) spherical hollow particles described in some papers, for example in [4], can be the result of additional crushing of drops in plasma. Such a crushing may be caused by high-speed plasma jets combined with lowering of the surface tension with the growth of temperature, and also by the high-temperature environment of a drop. As a mechanism of such a high-temperature crushing it is possible to offer the drop volume absorption of thermal radiation energy followed by boiling of a drop.

In paper [3] the theoretical comparative evaluations of compact (dense, solid) and hollow spherical particles behavior at different stages of spraying technology and in various processes during spraying were made. The dense spherical particle has the diameter d_0 and the hollow one has the diameter d_1 and a central spherical cavity with the diameter αd_1 . The value $\alpha = 0.7 \div 0.9$ is typical for real powders. As a result of consideration the following main conclusions were obtained. At the stage of aerodynamic classification the lower boundary of separation is higher for hollow particles by the factor of $(1 - \alpha^3)^{-0.5}$. Comparison of the powder's fluidity and the particles behavior at the stages of gas-dynamic acceleration and melting showed that the factor of magnification of the size for hollow particles is identical for all these cases and is equal to $(1 - \alpha^3)^{-1}$, that is the behavior of a dense particle with the diameter d_0 and a hollow one with the diameter $d_1 = d_0 / (1 - \alpha^3)$ is equivalent. It means the possibility of using coarser powder fractions in the process of thermal spraying. If the material of powder particles has a low thermal conductivity, which is typical for oxide powders, the factor of possible magnification of particle size for the main stage of thermal spraying, i.e. melting, may be as large as $(1 + \alpha + \alpha^2) / (1 - \alpha)$. This means that for $\alpha = 0.8$ possible particle size magnification is almost 7 fold.

The experience of using of spherical hollow oxide particles for thermal spraying is not extensive but obviously positive. It should be noted, that the powders used were of such chemical compositions which are not present in the nomenclature of the firms specializing in production of powders for thermal spraying. So, there is an experience of CeO_2 powder (see Fig. 1) spraying on a steel substrate. Fraction $100 \div 200 \mu\text{m}$ was used. Though the detailed study of the coating obtained was not carried out, visual and microscopic studying of the coating showed its satisfactory quality. It is necessary to note, that the melting temperature of CeO_2 as well as ZrO_2 exceeds 3000 K, but for deposition of a ZrO_2 coating by thermal spraying it is necessary to use particles with a size less than $60 \mu\text{m}$. So, the conclusion of paper [3] about possibility of the utilization of coarser powder fractions in the process of thermal spraying was confirmed.

There is a positive experience of production of spherical hollow particles of Nb_2O_5 and Ta_2O_5 by plasma spray pyrolysis. The powders of such a chemical composition for thermal spraying are not produced. On the basis of the available experience on plasmachemical treatment of fluoride solutions [5] and some additional experiments a method of producing Nb_2O_5 and Ta_2O_5 spherical hollow particles with the size of $100 \div 200 \mu\text{m}$ at a plasmachemical arc installation was developed. The attempt to produce such powders was

inspired by the desire to produce coatings from the above materials by thermal spraying. Simultaneously the attempts were undertaken to produce such coatings from powders obtained by traditional chemical methods, after preliminary selection of the fraction of $50 \div 100 \mu\text{m}$. A comparative study of thermal stability of Nb_2O_5 coatings, obtained from two different aforementioned kinds of powder was carried out. The coatings from the conventionally produced powder were hard to deposit because of bad fluidity and small utilization factor of the powder. Thin (0.2 mm) coatings obtained from such a powder peeled off at once or after one - two heat - cooling cycles. The powder specially obtained by plasma pyrolysis was much better sprayed and the resulting coatings were much more stable.

The powders produced by plasma pyrolysis usually contain about 1 % of anion impurity, even in the case when the process temperature is high enough to ensure total pyrohydrolysis. If to consider the process of thermal spraying, it becomes clear, that this anion impurity should not play an essential role. Really, the gaseous products formed during thermal spraying are rather harmful and require sanitary cleaning, therefore the addition of a certain amount of the anion component should not deteriorate the situation. During the particle melting salt impurities will transform into oxides. As only melted particles form coatings, the coating formed will consist of pure oxides. The loss of some percent of the material during this additional chemical purification will not play an essential role, as the powder utilization factor during the thermal spraying process is very seldom as high as 0.9.

Analysis of the experimental data and the theoretical evaluations allow to suggest using plasmachemical decomposition of solutions for production of oxide powders suitable for thermal spraying. The particles of such powders are hollow spheres with the size of $50 \div 200 \mu\text{m}$. The available experience justifies such an approach, especially for the case of materials, whose powders are not specially produced for the purposes of thermal spraying.

References

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