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Experience in plasma production of hollow ceramic microspheres with required wall thickness

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Abstract

With the example of zirconium dioxide, a process for the plasma production of hollow spherical powders with controllable shell thickness has been studied. The formation of hollow microspheres, or microballoons, is achieved through melting of an initial porous powder in the plasma jet of a DC plasma gun. Hollow microballoons 40 to 125 μm in size with shell thickness 2 μm and over were obtained. The experience in measuring the characteristics of hollow microspheres, namely their sizes, density, and wall thickness, is outlined. A procedure for preliminary and final classification of powders which enables the production of spheres with desired volumetric density and wall thickness is proposed.

Keywords: B. Porosity; C. Mechanical properties; D. ZrO_2; E. Thermal applications

1. Introduction

Hollow spherical (HOSP) powders are made up by spherical particles that contain a central gas-filled cavity concentric with the outer surface of particle – microballoons. Unlike void-free, or dense, powders, hollow microspheres are characterized, in addition to the outer particle diameter D, also by the wall thickness Δ. Such powders have gained widespread use, and they offer potential in many novel technological processes. Among such processes is the production of lightweight and buoyant materials [1], strong composite sound and heat insulators [2], heat-insulating paint coatings [3], lightweight proppants [4], radio transparent ceramics and electromagnetic interference isolation [5–7], explosives [8], catalysts [9], inertial fusion confinement targets [10,11], etc. Investigations into the possibility to extract helium out of natural gas [12] and to store hydrogen [13] using the selective gas permeability of ceramic hollow spheres are under way. In the majority of the new technologies, only the light weight, or low density, of the hollow powders is used. However, in some technologies stringent requirements are also imposed on the chemical composition of the spheres, their thermal stability, geometry, and mechanical strength. One example of successful applications of microballoons is the plasma spraying of thermal barrier coatings (TBC), in which the hollow structure of zirconia particles enables a reduction of the thermal conductivity of sprayed coatings without an increase in their total porosity [14,15]. The latter effect is due to more complete melting of zirconium dioxide particles in plasma [16], and also due to a unique flow pattern in the spreading hollow droplet [17,18].

Nowadays, the sol–gel methods, and also the precipitation of precursors and solutions, allow one to obtain hollows spheres of almost any desired size and chemical composition. Yet, difficult realization, high expenses, and the low product yield restrict the mass use of the methods. The main methods for many-ton production of hollow spheres are the grading of cenospheres [19] and the expansion of glass particles in a flame or in a high-temperature gas flow. Unfortunately, physical characteristics of aluminosilicate cenospheres are poorly reproducible, and they largely depend on the particular coal field from which the coal was excavated. On the other hand, glass powders have rather limited mechanical strength

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and a low melting point of 450–600 °C. Besides, those processes do not allow production of hollow microspheres from other ceramic materials.

Hollow microspheres of refractory ceramics can be obtained by spheroidization of a powder in a low-temperature (4–20 kK) plasma with throughput in excess of 20 kg/h [20]. The authors of [20,21] have attempted prediction of characteristics (density and shell thickness) of produced spheres on the assumption that the change of particle sizes in plasma processing is negligible, not exceeding 2–5%. However, later in [22] it was shown that the approach of [20,21] is inadequate, and the obtained hollow microspheres show a wide spread of shell thicknesses even if taken from narrow granulometric fractions.

The purpose of the present study was to introduce a method for plasma production of hollow ceramic powders with desired characteristics (outer particle diameter, wall thickness, and volumetric density).

2. Material and methods

Plasma spheroidization of powders was carried out in a nitrogen plasma jet produced by a linear DC plasma gun that was designed at ITAM SB RAS, Novosibirsk [20]. The process was held under atmospheric pressure using a standard regime ensuring complete particle spheroidization; this regime was as follows: plasma-forming nitrogen flow rate 30 slpm, arc current 150–200 A (voltage 180–190 V), thermal efficiency 60%, anode diameter 10 mm, feed rate of powder 6 kg/h. This provided average gas temperature at nozzle exit 6–8 kK, velocity about 300–400 m/s, and typical length of the plasma plume 200–250 mm. The powder was injected into the plasma jet using two radial injectors into the region under the plasma-gun nozzle exit [20]. The powder was processed in a plasmochemical water-cooled reactor whose volume was 30 l [21]. The plasma gun was connected to the upper part of the reactor. To the bottom part of the reactor, a powder receiver and a gas discharge hose were connected.

For the formation of hollow spheres, zirconia stabilized with 8 wt% yttria of Metco 204B or 204C grade powders (Sulzer Metco, USA), often used in application of TBCs by thermal spray methods, was employed. The feedstock powder was formed by agglomerates of glued grains; the sizes of the grains were smaller than 1 μm (Fig. 1a). The shape of the particles was roughly hemi-spherical, with a typical opening formed on one side of each particle as a result of the spray drying process.

The outside appearance of powder particles was examined with the help of an Evo MA15 scanning electron microscope and a Stereo Discovery V12 optical microscope (Carl Zeiss, Germany). After processing in plasma, the powder exhibited a high flowability, with its particles being shaped as spheres with a continuous surface without holes (Fig. 1b). The spheres had a crystalline structure possessing a higher mechanical strength in comparison with the initial glued agglomerates; as a result, long-term storage and transportability of the plasma-treated powder without destruction of its particles was possible.

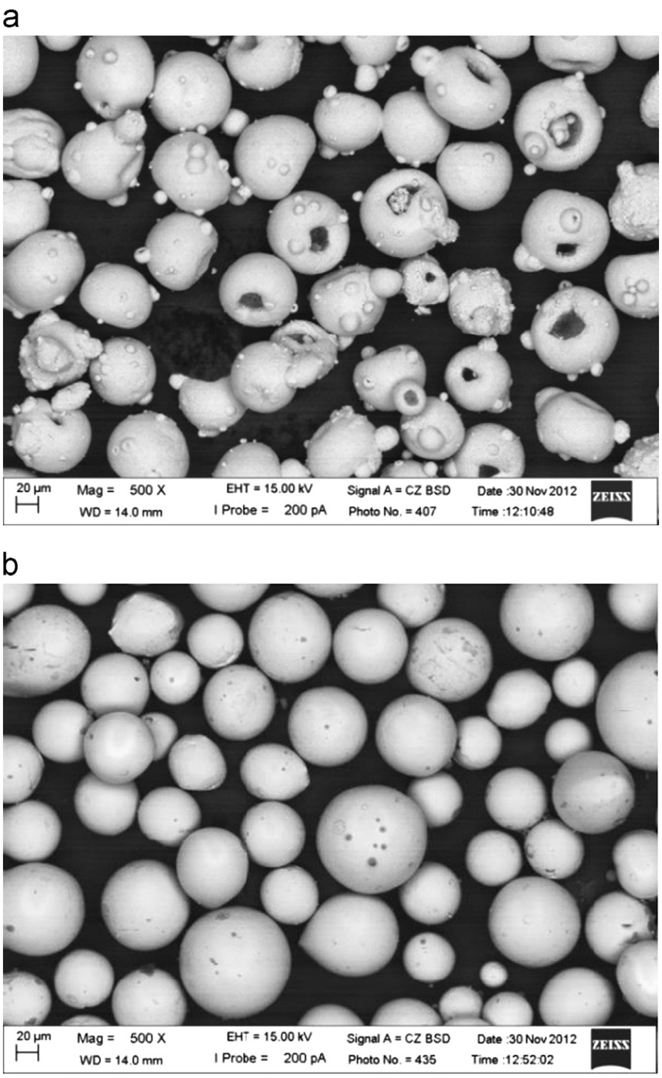

Fig. 1. SEM images of the ZrO_2 powder: (a) starting 204B powder and (b) final microballoons.

The XRD study was performed on a D8 Advance diffractometer (Bruker, Germany) using Cu radiation with wavelength 1.5418 Å. An analysis has showed that both feedstock powders were two-phase powders that consisted of the monoclinic phase of zirconia and the cubic form of yttria (Fig. 2, top). In all cases, after spheroidization in plasma the produced microballoons showed just reflections of the tetragonal phase of ZrO_2 (Fig. 2, bottom) with lattice constants $a=3.6175$ Å and $c=5.1665$ Å. In the processed powder, the phase Y_2O_3 was not observed because yttrium was incorporated into the lattice of zirconium oxide, thus stabilizing its tetragonal phase. This result is an important one for application of hollow powders in the field of thermal spray coating.

The granulometric grading of the powders was carried out by the size grading on braided sieves with mesh sizes 40 to 200 μm. Attempted use of laser-diffraction particle size analyzers SALD 2101 (Shimadzu, Japan) and LS 13 320 (Beckman Coulter, USA) has shown that those analyzer yielded rather inadequate data on the size distribution of hollow spheres. By