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SciVerse ScienceDirect
Journal of the European Ceramic Society 33 (2013) 3313–3324
www.elsevier.com/locate/jeurceramsoc

Atmospheric plasma spraying coatings from alumina–titania feedstock comprising bimodal particle size distributions

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Received 19 December 2012; received in revised form 19 April 2013; accepted 4 May 2013
Available online 15 June 2013

Abstract

In this work, Al_2O_3–13 wt% TiO_2 submicron-nanostructured powders were deposited using atmospheric plasma spraying. The feedstocks were obtained by spray drying two starting suspensions of different solids content, prepared by adding nanosized TiO_2 and submicron-sized Al_2O_3 powders to water. The spray-dried granules were heat-treated to reduce their porosity and the powders were fully characterised in both untreated and thermally treated state. Comparison with two commercial feedstocks was carried out. Characterisation allowed a temperature for the thermal treatment to be chosen on the basis of the sprayability of the feedstock and the preservation as much as possible of the submicron-sized structure of the unfired agglomerates.

Optimisation of the deposition conditions enabled the reconstituted powders to be successfully deposited, yielding coatings that were well bonded to the substrate. The coating microstructure, characterised by SEM, was mostly formed by a matrix of fully molten particles where the presence of semi-molten feedstock agglomerates was also observed.

Moreover, microhardness, toughness, adhesion and tribological behaviours were determined, and the impact of the granule characteristics on these properties was studied. It was found that changing the feedstock characteristics allows controlling the coating quality and properties. In general, good mechanical properties were obtained using a feedstock comprising a binary mixture of submicrometric Al_2O_3 and nanometric TiO_2 particles in the spray-dried powder.

Keywords: Suspensions; Al_2O_3–TiO_2; Nanoparticle; Rheology; Spray-dried powders

1. Introduction

Thermal spray, and particularly atmospheric plasma spray (APS), is one of the most economical and viable processes to obtain coatings at an industrial scale, given its high deposition rates and that there is no need for special atmospheric or chemical chambers. Additional advantages are the durability and high thickness of the coatings.

The manufacture of nanostructured coatings would provide enhanced properties over those obtained for micronic or submicronic ones. In order to obtain nanostructured coatings it is necessary to use nanoparticles as raw material. However, nanoparticles need to be reconstituted to a sprayable size in order to use regular powder feeders as well as to provide a route to safe handling of nanoparticles.[1] Reconstitution generally takes place by spray drying of a nanoparticle suspension and, frequently, thermal treatment (partial sintering) of the resulting granules.[2]

Although many authors have addressed the role of slurry formulation on the characteristics of the ceramic granules and many others have obtained spray-dried powders for thermal spraying,[3,4] most papers using nanostructured spray-dried feedstock only mention the agglomeration process without providing a complete experimental study of nanoparticle suspension preparation, spray-drying operation, or thermal treatment of the resulting agglomerates. Thus, the correlation between agglomeration process variables, agglomerate characteristics, and coating microstructure and properties is far from being well established.

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http://dx.doi.org/10.1016/j.jeurceramsoc.2013.05.009

Al_2O_3–TiO_2 coatings fabricated with nanopowders show very promising bonding strength and wear resistance when compared with conventional feedstock as reported elsewhere.[5,6] Although many research efforts have been made to pass from the micro-scale to either the nano- or the submicron-scale using both powders or liquids as feedstock,[7,8] few attempts have been made to use feedstocks in which mixtures of different particle size distributions, e.g. submicron–nano sized particles, are present. The use of a bimodal distribution of submicron-nano particles, comprising the precursor suspension of the spray-dried powder, can give rise to significant benefits during the suspension processing, i.e. higher solids content and lower viscosity leading to better properties in the resulting feedstock agglomerates, such as higher agglomerate bulk density and improved powder flowability.[9,10] This is particularly interesting for alumina suspension due to the intrinsic difficulties associated with the preparation of concentrated nanoparticle suspensions of alumina as reported elsewhere.[11] The relationship between these improved agglomerate feedstock characteristics and the final coating properties has been scarcely treated in the literature.[10] In this respect, we have also recently reported improved photocatalytic activity in APS TiO_2 coatings when using a mixture of nano and submicrometric particles in the spray-dried feedstock.[12] Much higher density agglomerates were obtained which led to better properties in the final coatings.[11,12]

In previous research by the authors, it was found that the nanostructured spray-dried agglomerates obtained from concentrated Al_2O_3–13 wt% TiO_2 suspensions yielded coatings with lower void content than those obtained using powders from less concentrated suspensions.[11] However, feedstocks made up of powders with bimodal particle size distribution (submicronic–nanometric particles) were not explored.

This work deals with the relationship between the reconstituted granule characteristics and the properties of Al_2O_3–13 wt% TiO_2 coatings obtained from spray-dried feedstocks made up of TiO_2 nanoparticles and Al_2O_3 submicrometric particles with a view to addressing the potential benefits of the use of bimodal feedstocks. Complete characterisation of feeding powders (FEG-ESEM, granule size distribution, flowability and apparent density) and of newly developed coatings (microstructure by SEM and mechanical properties such as microhardness, toughness, wear rate and cohesion strength) was performed. The expected benefits of the use of submicron-sized alumina (instead of nanosized alumina) together with nanosized titania comprising the spray-dried feedstock can be then summarised as follows: easier suspension preparation and handling with the achievement of much higher solids concentration, better feedstock characteristics associated with an (expected) higher agglomerates density and much lower feedstock cost.

2. Experimental

2.1. Feedstock preparation and characterisation

The following commercial powders were used as starting materials: (1) a submicron-sized, high purity α-Al_2O_3 (Condea-Ceralox HPA-0.5, Sasol, USA) with a mean particle size of 0.35 μm and a specific surface area of 9.5 m^2/g; and (2) a nanosized TiO_2 powder (Aeroxide® P25, Degussa-Evonik, Germany) with an average primary particle size of 40 nm, a specific surface area of 50 m^2/g, and a relative ratio of anatase:rutile phases of 3:1.[13] Mixtures of submicronic alumina and nanometric titania were always prepared at a relative weight ratio of 87:13. Finally, and for comparison purposes, two commercial feedstocks with the same Al_2O_3:TiO_2 weight ratio, were also deposited: a conventional microstructured one (Metco 130, Sulzer Metco, Germany), referred as MC, and a nanostructured one (Nanox™ S2613S, Inframat Advanced Materials, USA), referred as NC.

The colloidal stability of aqueous suspensions of the TiO_2 nanopowder as well as the coarser alumina powder has been previously evaluated by zeta potential measurements.[9] This information allowed choosing the most adequate nature and proportion of dispersant so as to subsequently prepare high solids content suspensions. Thus, concentrated suspensions were prepared to solid contents of 30 vol.% and 50 vol.% (i.e. at 67 and 80 wt%, respectively) using deionised water. A commercial polyacrylic acid-based polyelectrolyte (DURAMAX™ D-3005, Rohm & Haas, USA) was used as a deflocculant. This was supplied as an aqueous solution of polyacrylic acid (PAA) with 35 wt% active matter of PAA $[(C_3H_4O_2)_n]$ and an average molecular weight of 2400. Studies elsewhere have shown that this deflocculant is suitable for obtaining concentrated suspensions of both studied materials.[13,14] The suspensions were prepared by adding first the PAA required to disperse all the particles (4 wt% PAA in relation to the titania content and 0.3 wt% PAA in relation to the alumina content). The foregoing PAA contents refer to the active matter concentration. After that, the titania nanopowder was added and homogenized with sonication for 1 min and subsequently the alumina powder was dispersed (without sonication). The mixture was then kept for 15 min under mechanical stirring.

It was not necessary to use a binder for spray-drying. In fact, spray-dried granules with adequate mechanical strength were obtained from the 30 vol.% and 50 vol.% suspensions (hereinafter feedstock AsTn30 and AsTn50, respectively) in a spray dryer (Mobile Minor, Gea Niro, Denmark) with a drying capacity of 7 kg water/h as set out elsewhere.[11] Granule size distribution was measured by laser diffraction (Mastersizer, Malvern, UK). Agglomerate apparent density was calculated from powder tapped density by assuming a theoretical packing factor of 0.6, which is characteristic of monosize, spherical particles.[15] Powder flowability was evaluated in terms of the Hausner ratio, determined by dividing powder tapped density by powder apparent density.[15] Free-flowing powders have a Hausner ratio <1.25.

In order to obtain denser granules, the spray-dried powders were heat treated in an electric kiln at a temperature rate of 25 °C/min to different maximum temperatures, which depended on the powder sample, with soaking time of 60 min.[11] The main objective of the heat treatment is to enhance the mechanical strength of the agglomerates and to reduce their shell porosity meanwhile the submicro/nano-structure of the feedstock