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Modified solution combustion route for the preparation of plasma sprayable ceria powder

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Abstract

Plasma sprayable grade ceria powder was prepared by the solution combustion method. This is the first report on the application of solution combustion for the synthesis of plasma sprayable grade oxide powders. The fuels and fuel ratios used in the solution combustion were modified to achieve adequate flowability. It was found that when a mixture of fuels like glycine and ammonium acetate was used, the combustion process yielded larger agglomerates. Phase purity of the powders was confirmed by powder XRD. The morphology of the particles was determined by scanning electron microscopy.

Keywords: A. Powders: chemical preparation; B. X-ray methods; B. Electron microscopy; D. CeO_2

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are considered one of the most promising power generation technologies for the future because of its high efficiency, low emission and its ability to utilize a wide number of carbonaceous fuels [1]. In order to use cobaltite perovskite type oxides as cathode material for reduced temperature SOFCs, a thin film of doped ceria has been proposed as a protective layer on a stabilized zirconia electrolyte [2]. Thermal spray, especially atmospheric plasma spray (APS) [3] seems to be an economically attractive and effective technique for industrial production of SOFC due to its advantages such as low cost, easy operation, high deposition efficiency, wide selection of materials, etc. [4,5]. The plasma spray technology requires powder with good flowability and large particle size (5–200 μm) [6]. Although extensive studies have been carried out on the chemical synthesis of ceramic oxide powders, only few efforts have been directed towards preparing chemically uniform oxide powders for plasma spray coatings. Most of the methods reported in the literature employ an additional agglomeration step like spray drying to get plasma sprayable powders which makes these processes more expensive and laborious [6]. Among the large number of techniques employed for the synthesis of oxides, solution combustion synthesis is unique and highly versatile [7].

To the best of our knowledge, there are no reports on the preparation of freely flowing oxide powders suitable for plasma spraying in a single-step using the solution combustion technique. In this communication, we report the combustion synthesis of plasma sprayable grade ceria powder.

2. Experimental

In a typical experiment, ceria-1 was prepared from solution combustion as follows: a Petri dish containing stoichiometric amounts of ceric ammonium nitrate (10 g) and glycine (3.6 g) with O/F unity ratio was introduced into a preheated muffle furnace (~350 °C). The solution boiled, followed by frothing and flaming combustion. Ceria-2 was prepared by the combustion of 10 g of ceria ammonium nitrate and 2.7 g glycine corresponding to (3/4) the stoichiometric weight of fuel. For the preparation of ceria-3, the glycine amount was further reduced to (1/2) that of stoichiometric amount of fuel. Ceria-4 powder was prepared from the combustion of a redox mixture containing 10 g ceric ammonium nitrate, 1.8 g glycine (corresponding to (1/2) the stoichiometric amount of fuel such that O/F = 1) and 1.53 g ammonium acetate (corresponding to (1/2) the stoichiometric amount of fuel such that O/F = 1).

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X-ray diffraction studies were carried out on a Bruker-D8 diffractometer equipped with a VÅNTEC–1 detector with copper Kα radiation (λ = 1.5418 Å). Microstructure of as-synthesized powders was characterized by a Leo 440I Scanning Electron Microscope (SEM).

3. Results and discussion

The combustion was flaming type with glycine and the reaction was very violent resulting in the flying of fine ceria from the container. To avoid the loss of ceria powder, the glycine amount was reduced to (3/4) and half that of the stoichiometrically calculated fuel amount. When the glycine amount was reduced from stoichiometric ratio to (3/4) the combustion reaction was controlled and the flying of powders was reduced. When the glycine amount was further reduced to (1/2), the flaming nature of the combustion reaction was further reduced but the powder contained traces of black particles. In order to get rid off the carbon, fuel like ammonium acetate was used. Assuming complete combustion, the theoretical equation for the formation of ceria using above fuels and fuel ratios, the chemical reactions can be written as follows.

Assuming complete combustion, the theoretical equation for the formation of ceria-1 using stoichiometric amounts of glycine is written as follows:

$$3(NH_4)_2Ce(NO_3)_6 + 8C_2H_5O_2N \rightarrow 3CeO_2-1 + 8NH_3 + 20H_2O + 9N_2 + 6NO_2 + 16CO_2 \quad (1)$$

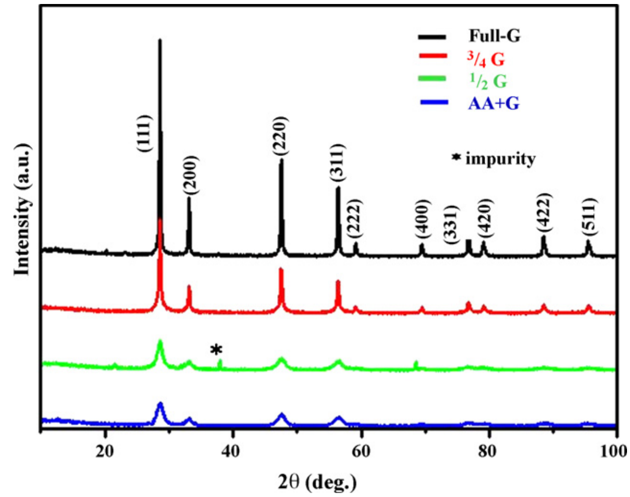

Fig. 1. Powder XRD patterns of ceria powders prepared using various amounts of fuel and fuel mixture (AA, ammonium acetate; G, glycine).

In the case of (3/4) fuel, we assume that since the fuel is reduced it is deprived of oxygen and it takes up atmospheric oxygen for the formation of phase pure ceria-2.

$$(NH_4)_2Ce(NO_3)_6 + 2C_2H_5O_2N + O_2 \rightarrow CeO_2-2 + 2NH_3 + 6H_2O + 2N_2 + 4NO_2 + 4CO_2 \quad (2)$$

For the preparation of CeO_2-3, with (1/2) the glycine fuel we assume the formation of carbon despite the use of atmospheric

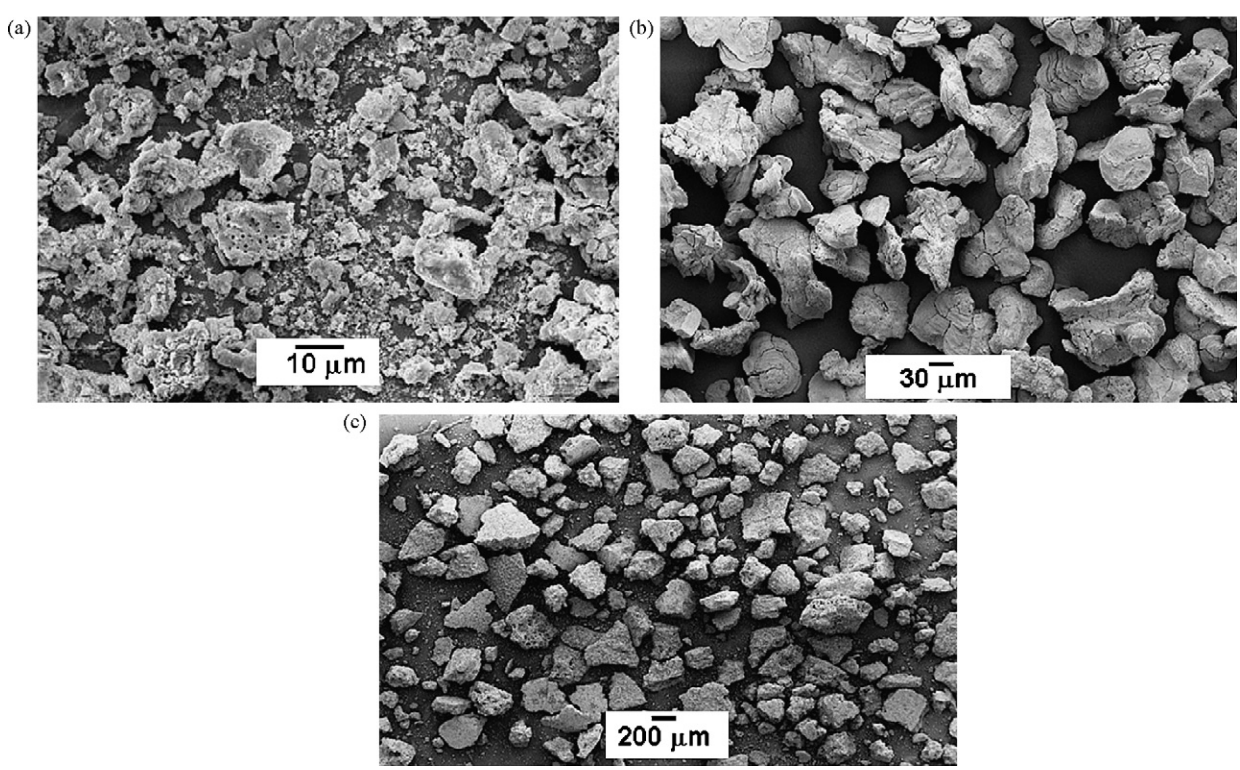

Fig. 2. SEM images of combustion synthesized ceria powders (a) (3/4) glycine, (b) (1/2) glycine and (c) mixture of ammonium acetate and glycine.

oxygen. The theoretical equation may be written as follows:

$$(NH_4)_2Ce(NO_3)_6 + 4C_2H_5O_2N + (17/2)O_2 \rightarrow 3CeO_2 - 3 + 6NH_3 + 13H_2O + 8N_2 + 6NO_2 + 7CO_2 + C \quad (3)$$

Using mixture of fuels glycine and ammonium acetate, the theoretical equation for the formation of phase pure ceria-4 can be written as follows:

$$2(NH_4)_2Ce(NO_3)_6 + 4C_2H_5O_2N + CH_3COONH_4 + 4O_2 \rightarrow 2CeO_2 - 4 + 5NH_3 + 14N_2O + 4N_2 + 8NO_2 + 10CO_2 \quad (4)$$

It is interesting to note that the number of gases evolved per mole of ceria for the above four equations are 19.66, 24, 14.33 and 20.5 moles, respectively. By decreasing glycine to half and adding ammonium acetate has resulted in almost equal number of moles of gases per mole of ceria as that of stoichiometric amount of glycine.

The powder XRD patterns of ceria prepared using different combinations of fuel are shown in Fig. 1. The XRD patterns confirm the formation of phase pure ceria without any impurities for full, (3/4) and mixture of fuels. It is apparent from the XRD patterns that as the fuel amount is reduced, the full width at half maxima (FWHM) of ceria powders is reduced. The XRD pattern of ceria powder prepared using mixture of fuels exhibited more line broadening indicating nanosize nature of the crystallites. The crystallite sizes as calculated from XRD line broadening using Scherrer formula was 36, 25, 6 and 5 nm, respectively, for ceria-1, -2, -3 and -4. As the exothermicity was reduced by decreasing the fuel amount, the crystallite size decreased. Although the crystallite size is smaller for ceria-4, the particles are agglomerated.

From the SEM images (Fig. 2), it is evident that as the glycine fuel amount was reduced, the % of agglomerated particles increased. The powder prepared using mixture of fuels exhibit blocky angular shape particles which are useful for plasma spraying (Fig. 2c). The agglomerates prepared using (1/2) glycine were softer compared to the ones prepared using mixture of glycine and ammonium acetate and are not suitable for plasma spraying. The flowability of the powder as measured according to ASTM B213-97 was about 100 s/50 g. The flowability is less compared to commercial samples; this may be due to the fact that in the present study we have not done any sieving of the very fine particles. There is a further scope for improving the flowability and morphology of the particles by changing the fuels and fuel ratios of the redox mixture. The flowable ceria powder will be used for plasma spraying and the results will be published. The probable mechanism for the formation of blocky angular shape particles will be explored.

4. Conclusions

The versatility of the solution combustion technique for the preparation of plasma sprayable grade ceria powder was elucidated. The use of fuel like ammonium acetate along with reduced glycine not only facilitated the formation of a pure ceria phase, reduced particle size but also yielded plasma sprayable grade ceria powder. There is a further scope for improving the flowability of the powders by modifying the redox mixture used for the solution combustion synthesis.

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