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Highly sinterable nanocrystalline yttria powders fabricated by solution combustion synthesis

Choong-Hwan Jung* and Ji-Yeon Park

Nuclear Materials Research Division, Korea Atomic Energy Research Institute, 1045 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Rep. of Korea

Nano-sized yttria powders were synthesized by solution combustion synthesis with glycine as a fuel. The powders were directly synthesized with a stoichiometric oxidant-to-fuel ratio in an air atmosphere without a calcination process and they were characterized by X-ray diffraction, a particle size distribution, SEM and TEM. The best powder properties were observed in the powders with a glycine-to-nitrate ratio of 1 : 1.66. This product had a crystallite size of about 31 nm with a high surface area of 38 m^2/g. The sintering behavior of the powders was also studied using a different process. Solution combustion synthesis was shown to be a practically viable process to prepare nano-sized and sinterable yttria-based ceramics.

Key words: Yttria, Combustion, Fuel, Glycine, Nano.

Introduction

Y_2O_3 (yttria) has potential applications because of its chemical stability, refractoriness with a high melting point (2410 °C), absence of a phase transition form, and good thermal properties. Because of its high chemical stability and refractory nature, it has a wide range of applications, e.g., high-temperature chemical-resistant substrate, crucibles for melting reactive metals and nozzles for jet casting molten rare earth-iron magnetic alloys. In addition, transparent yttria ceramics are useful for optical applications such as high pressure sodium lamp arc tubes, IR windows in heat seeking rockets, and as laser host materials [1-6].

The synthesis of nanocrystalline ceramics is an advanced field of processing technology. In general, as the particle size is reduced to a nano-regime, the physical-chemical properties show a gradual movement from solid-state matter to atomic scales. These materials can show greatly different optical, electronic and catalytic properties when compared to their macro-crystalline ones. In view of this point, yttria still is attractive for researching newer and better processing routes for its synthesis in the nano-crystalline range. For practical applications of yttria-based ceramics, the synthesis of a yttria powder with controlled powder characteristics is necessary to obtain a dense sintered product at a lower sintering temperature. Various chemical routes such as co-precipitation and sol-gel are known to yield sinter-active materials. Highly purified yttria powders obtained after the thermal decomposition of yttrium precursors require temperatures in excess of 1600 °C for sintering, and these synthesis methods are involved and require long processing times and expensive chemicals [7-9].

Among the available wet chemical processes, a solution combustion synthesis technique is capable of producing ultra-fine powders of oxide ceramics in a shorter time and at lower calcination temperature with improved powder characteristics. Solution combustion synthesis has been used with various fuels to synthesize nanocrystalline yttria; however, a correlation between the powder properties and processing is still not well understood. In the present study, we have carried out a synthesis process with a ratio of oxidant-to-fuel, and examined the subsequent changes in the powder characteristics and sintering behaviors of the synthesized powders [10-16].

Experimental Details

Yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$), glycine (NH_2CH_2COOH) and HNO_3 were used as starting materials. According to the formula, stoichiometric amounts of yttrium nitrate and glycine were first weighted and HNO_3 was added at the required molar ratios in a minimum volume of de-ionized water to obtain transparent aqueous solutions [17]. These solutions, after a thermal dehydration (at 300 °C on a hot plate to remove the excess solvent), became highly viscous liquids. As soon as the viscous liquids were formed, the temperature of the hot plate was increased to 400 °C. At this stage, the viscous liquids swelled and autoignited, with a rapid evolution of a large volume of gases to produce voluminous powders. Since the time for the auto-ignition to exist is rather small (<10 s.), to fully react traces of unreacted glycine and nitrates, the powders obtained after a combustion synthesis were heat-treated at 500 °C for 2 h to obtain pure and well-crystallized yttria powders. X-ray diffraction studies were carried out on the combustion synthesized powders,

*Corresponding author:
Tel : +82-42-868-8567
Fax: +82-42-862-5496
E-mail: chjung1@kaeri.re.kr

for phase identification and crystallite size estimation. The microstructure of the as-synthesized powders was investigated using a scanning electron microscope. Bright field TEM was used for an estimation of the size of the primary crystallites, and the nature and extent of the aggregation.

Results and Discussion

Generally, the solution combustion synthesis provided homogeneous phases with an excellent crystallinity due to the high temperature arising from the extreme exothermal reaction. Therefore, both the types and amounts of the fuel and ratios (F/O) have to be considered carefully because they play an important role in the total reaction characteristics. According to the principles of the propellant technology for a redox reaction between a fuel and an oxidizer, where a cation such as carbon, hydrogen and oxygen acts as a fuel and an anion of a metal nitrate such as an oxygen acts as the oxidizer, the ratio of the oxidizing valence to the reducing valence should be unity [14, 17].

In this system, to satisfy this stoichiometric ratio, the yttrium nitrate (oxidizing valence = –15) to glycine (reducing valence = +9) molar ratio was found to be 1 : 1.66. The reactivity of the solution combustion is dependent upon the molar fuel-to-oxidizer ratio, and the optimal ratio depends on the desired final composition. The relation of a given ratio to the optimal ratio is known as the elemental stoichiometric coefficient (ESC, the fuel-stoichiometric composition ndicates $\Phi_e = 1$). Table 1 shows the as-synthesized powder properties. The crystallite size was calculated by X-ray line broadening using the Scherrer formula. The average agglomerate size, surface area, observed flame temperatures and the moles of gases

(calculated from the stoichiometric composition equation; $9\{Y(NO_3)_3{\cdot}6H_2O\} + 15(H_5NC_2O_2) \rightarrow 9/2Y_2O_3 + 30CO_2 + 183/2\ H_2O + 21N_2 + 5O_2$) are also given in Table 1. In general, the stoichiometric compositions provide higher exothermic reactions, thus increasing the crystallite size and agglomerates arising from a local partial coarsing among the active nano-sized primary particles produced during the solution combustion, thereby reducing the surface area.

Fig. 1 shows the XRD pattern of the as-synthesized yttria powder. It can be seen that crystalline yttria powder was readily obtained without further calcinations steps, which is a major advantage of this process because a high temperature calcination process usually results in hard-agglomerated powders. Thermogravimetric analysis (TGA) of the as-synthesized powder indicated a little weight loss (~ 2.0%) up to 1400 °C. The BET surface area of the combustion synthesized powder was 38.04 m^2/g. The primary particle size was calculated to be 31 nm, which agreed well with the value calculated by the X-ray line broadening.

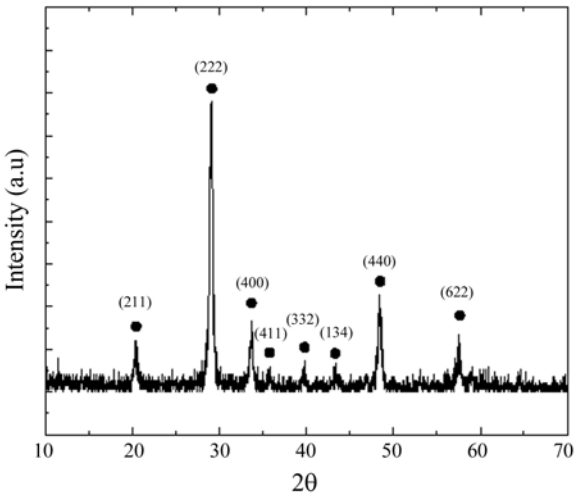

Fig. 1. X-ray diffraction pattern of yttria powder prepared by solution combustion synthesis.

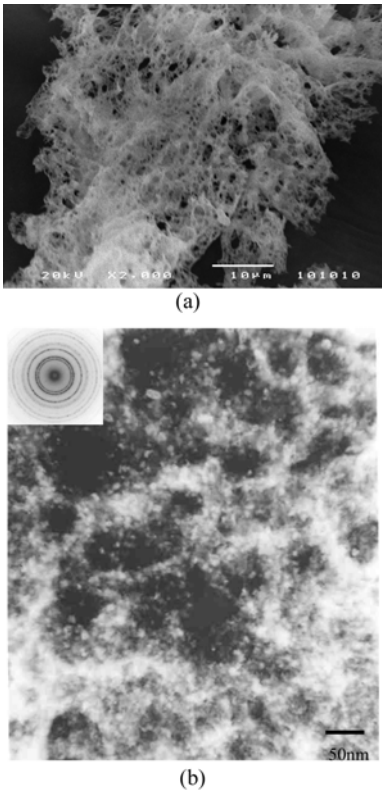

Fig. 2. SEM (a) and TEM (b) images of the as-synthesized powder.

A SEM micrograph of the as-synthesized powders processed with glycine is shown in Fig. 2(A). It seems to

Table 1. Powder properties

Oxidant- to-fuel ratio	Φ_e (ESC)	Phase	No. of moles of gases	Crystalline size	Ave. agglo. size by light scattering	Surface area (m^2/g)	Reaction time	Observed flame temp.
1 : 1.66	1.00	yttria	16.39	31 nm	0.704 μm	38.04	8 sec	1232 °C

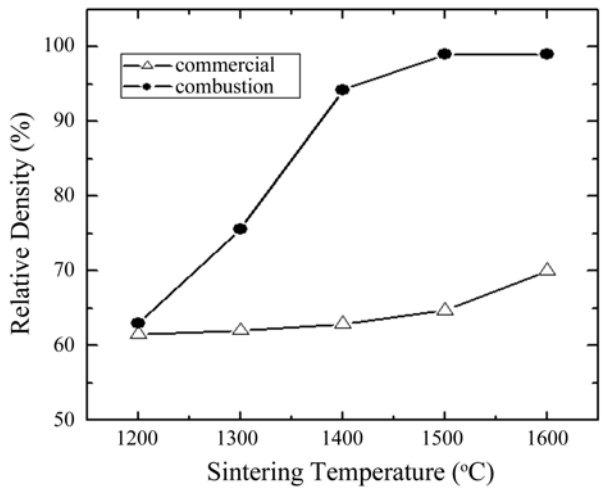

Fig. 3. Sintered densities of Y_2O_3 ceramics prepared by different powder processing routes.

form weak agglomerates with a fragile network and a foamy-porous structure, which is the typical microstructure of combustion synthesized powders. Fig. 2(B) shows a TEM micrograph, it can be seen that the particle size is essentially less than 20 nm, although the particles do not appear to be well separated. Here the aggregated behavior of the particles become much clearer. Thus it could be suggested that the combustion synthesized powders are in an agglomerated form. It was shown earlier that these agglomerates are soft in nature and can be easily broken by weak forces such as ultrasonication.

The sintered densities of yttria, with the sintering temperature, are shown in Fig. 3. The commercial yttria powder was only sintered to 70% of (theoretical density) at 1600 °C for 2 h, whereas the combustion as-synthesized powder was sintered to 98% of TD at 1500 °C for 2 h. As expected, the highest density (98% of TD) was observed for the combustion synthesized powders, at as low a temperature as 1500 °C, owing to its superior powder properties. It can be inferred that the ultra-fine and highly active nature of this powder assisted in the sintering behavior when compared to commercial powders.

Conclusion

The yttria nano-sized powders in this study were synthesized by a solution combustion synthesis process. There is an optimum oxidant-to-fuel molar ratio (1 : 1.66) in the present case, which provides the best powder characteristics. The as-synthesized yttria powders had a fine size and a good sinterability, which could reach at 98% of TD at a temperature as low as 1500 °C. The solution combustion synthesis process was proven to be a simple approach to prepare high quality yttria-based ceramics.

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