

EFFECTS OF PVA POLYMER TYPE AND CALCINATION TEMPERATURE ON SYNTHESIS OF NANOCRYSTALLINE YTTRIA POWDER BY POLYMER SOLUTION ROUTE

Nano-sized yttria (Y_2O_3) powders were synthesized by a polymer solution route using polyvinyl alcohol (PVA) as an organic carrier. The PVA polymer affected the dispersion of yttrium ions in precursor sol. In this study, three kinds of PVA polymer (different molecular weight) were applied for synthesis of yttria powder. The PVA type as well as calcination temperature had a strongly influence on the particle morphology. Single crystal nano wire particles were observed at the temperature of polymer burn out range and the size was dependent on the PVA type. The stable, fully crystallized yttria powder was obtained through the calcination at 800°C for 1 h. The yttria powder prepared with the high weight PVA (MW: 153,000) revealed a particle size of 30 nm with a surface area of 18.8 m²/g.

Keywords: Yttria, PVA, Nanocrystalline, Synthesis, Nano wire

1. Introduction

Yttria has a wide range of applications, such as a high-temperature chemical-resistant substrate, crucibles and nozzles for melting reactive metals and jet casting molten. In addition, as an optical and transparent yttria ceramic, it transmits light well in the infrared range of 1.0 to 8.0 μm wavelength. Such a high infrared transmission together with good resistance to erosion and thermal shock make the material ideal for developing protection missile domes as well as infrared and lasers sensors [1-6].

The synthesis of nano-sized ceramic powders is an advanced field of a processing technology [7-9]. Nano-scale ceramics can show greatly different optical, electronic or catalytic properties when compared to their macro-crystalline ones. In view of this point, yttria still has attractions for investigating newer and better processing routes for its synthesis in a nano-crystalline range. For the practical application of yttria-based ceramics, the synthesis of yttria powders with controlled characteristics is necessary to obtain a dense sintered product at a lower sintering temperature [10,11].

There are several methods reported for the processing of yttria ceramic powders. They include precipitation, hydrothermal, co-precipitation, glycothermal treatment, electro-spray-pyrolysis and sol-gel processing [10,11]. Each one of these methods has its merits and demerits. Especially, a polymer solution route which uses polyvinyl alcohol (PVA) is capable of producing ultra-fine powders of oxide ceramics in shorter time and at a lower calcination temperature with improved powder characteristics [12-15]. A polymer solution synthesis has been used with PVA to

synthesize nanocrystalline yttria. As a previous study, the effects of PVA content on the yttria powder morphology and powder specific surface area were studied [16]. The PVA content also had an influence on the synthesis behavior and final powder microstructure. The yttria powder synthesized from the PVA content of 4:1 had a crystallite size of about 15 nm with a high surface area 34.71 m²/g.

In the present study, we have carried out a synthesis process with the effect of molecular weight of PVA, and examined the subsequent changes in the powder morphology and crystallization behavior. In this study, the nano-yttria powders are made by a steric entrapment route using PVA. By using this method, the PVA types strongly affected the entrapment mechanism, which can control the chemical and physical characteristics of precursor sol.

2. Experimental

Yttrium nitrate, ($Y(NO_3)_3 \cdot 9H_2O$, reagent grade, China) was used as a source of yttrium cations. The nitrate salt was dissolved in de-ionized (DI) water. Once the cation source was completely dissolved, 5 wt% PVA solution was added to the sol solution. PVA (Air Products and Chemicals, Inc., Airvol Series, PA, USA) was dissolved in DI water to prepare the PVA solution. The PVA mixing content was 4:1 ratio. The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 4 times more positively charged valences from the cations than those from the potentially negatively charged (OH) functional groups of the polymers. The polymeric

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long chains have hydroxyl groups in solution. Hence, one PVA monomer, which has one hydroxyl (OH) functional group, can be used as a unit for the calculation of the PVA content. The PVAs which have different molecular weight (MW) of 9,000, 40,000 and 153,000 were used for the preparation of Y_2O_3 precursor. Water in the precursor sol was evaporated by continuous stirring during heating on a hot plate. The resulting gel-type precursors were completely dried in air for 24 hours at 120°C. Each of the ground precursors were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. Each of the components was calcined at a heating rate of 3 °C/min. The crystallization behavior of each of the calcined powders was studied as a function of the temperature and PVA content, using an X-ray diffractometer with $CuK\alpha$ radiation. The pyrolysis and decomposition behavior of the precursors were monitored by DTA/TGA in an air atmosphere up to 1000°C at a heating rate of 10°C/min, in an air atmosphere. The specific surface area of the as-synthesized was obtained by five-point BET analysis from nitrogen gas adsorption. All the samples for testing were kept in a dry oven to prevent the hydration of the powders. The crystallized powders were examined by TEM for study of the powder morphology and size distribution.

3. Results and discussion

The organic-inorganic precursors employing yttrium cations and PVA polymer were formed by the development of foam during the stirring and drying process. The foams were generated during the evolution of NO_x gases from the decomposition of the nitrates. The simultaneous DTA/TGA result of the powder precursor gel prepared with the PVA (MW : 153,000) from room temperature to 1000°C is shown in Fig. 1. A notable exothermic peak was observed at 200°C and several other exothermic peaks were detected in the range of ~500°C. The accompanying weight loss was observed through two steps (100 ~ 400°C and 400 ~ 600°C). Beyond 600°C, the weight loss was not observed any more. The first weight loss with the main exothermic peak was due to the evaporation of water and the pyrolysis of nitrate. The first weight

loss was continuously followed by the decomposition of the polymer chain of the PVA. The oxidation of carbons occurred with another significant weight loss in the temperature range of 400 ~ 600°C. Finally, the oxidation of residual carbons occurred gradually with the complete disappearance of weight loss at 600°C.

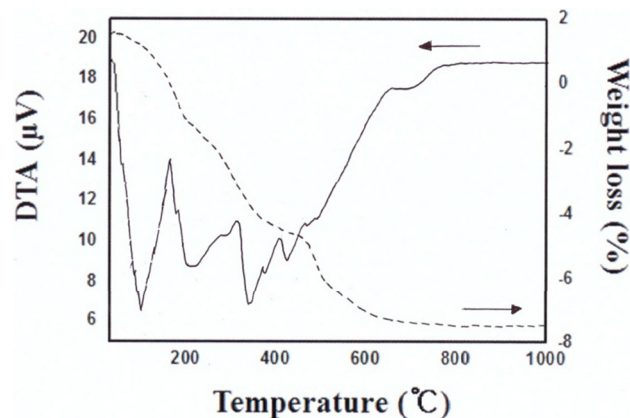


Fig. 1. Simultaneous DTA/TGA result of precursor gel prepared with PVA (MW : 153,000) from RT to 1000°C

Fig. 2 shows the XRD results of the precursor prepared with PVA (MW: 153,000) according to different calcination temperatures. The precursor calcined at 400°C showed carbon compound and yttrium metal with a small peak identifying yttria phase. At 600°C, developed yttria phase was observed with less amount of the carbon compound and yttrium metal. The precursor was fully crystallized to yttria phase without any other phases at the temperature of 800°C, at which all organic precursors are burned out completely. It is speculated that the oxidation reaction for polymer burn-out in the step of the removal of residual carbon provided enough oxygen source to decompose the carbon compound during the calcination process. These effects resulted in the impurity free, fully crystallized yttria in the PVA solution process.

The TEM morphologies of the calcined powders at 400°C according to different PVA molecular weight are shown in (Figs. 3-5). The powder morphology was significantly changed with different PVA molecular weight. The powder prepared with

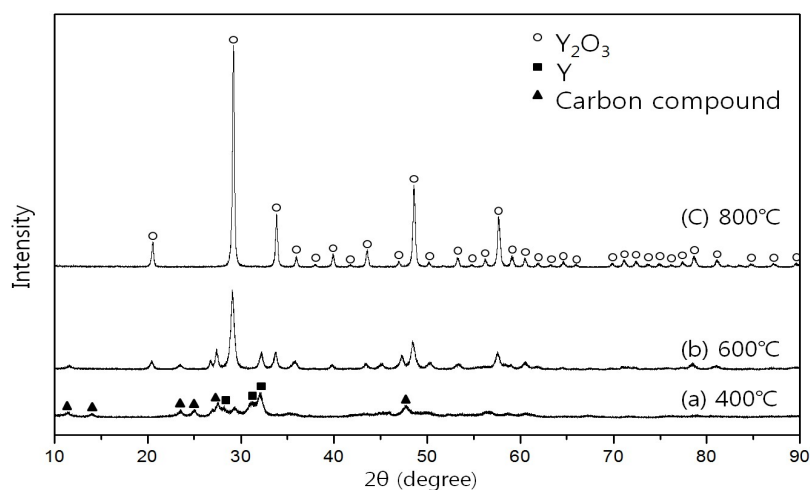


Fig. 2. XRD patterns of precursor gels, prepared with PVA (MW: 153,000), calcined at 400°C, 600°C and 800°C

low MW PVA revealed a relatively small particle size of about 10 nm (Fig. 3). The nano-sized crystals were observed through a high resolution TEM image. In the microstructure of the powder prepared with medium MW PVA (Fig. 4), wire – type single crystals were observed with some amorphous phases. The nano wire particles showed clear single crystal atom arrangement. Larger nano wire particles as well as amorphous-type particles were observed in the microstructure of the powder prepared with high MW PVA. In comparison with the nano wire particles derived from medium MW PVA, the size and crystallinity were increased. From the XRD results (Fig. 2), the nano wire may be

a single crystal of metal yttrium. The effect of PVA molecular weight on powder morphology was notable in the synthesis of yttria powder at low temperature. This means that the steric entrapment mechanism occurred in the precursor sol is strongly affected by the PVA polymer molecular weight in the synthesis behavior of yttria powder, in particular on the beginning of the synthesis process accompanying polymer burn out.

TEM micrograph of fully crystallized yttria powder at 800°C, prepared with high molecular weight PVA (MW: 153,000) is presented in Fig. 6. The synthesized yttria powder was about 30 nm in size. Although the powders appeared soft

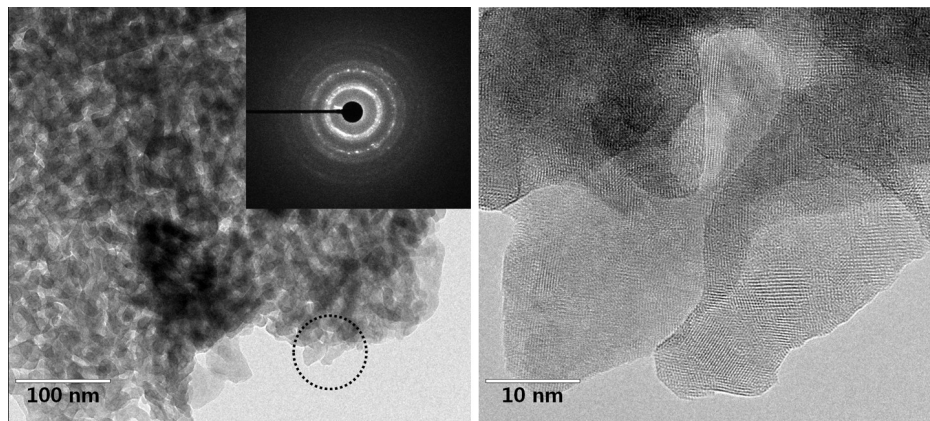


Fig. 3. TEM photographs and SAD of calcined powder at 400°C, prepared with low molecular weight PVA (MW : 9,000)

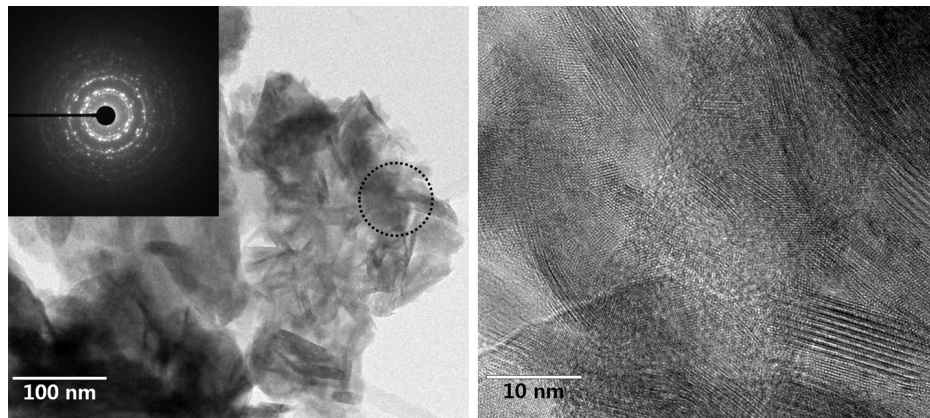


Fig. 4. TEM photographs and SAD of calcined powder at 400°C, prepared with medium molecular weight PVA (MW : 40,000)

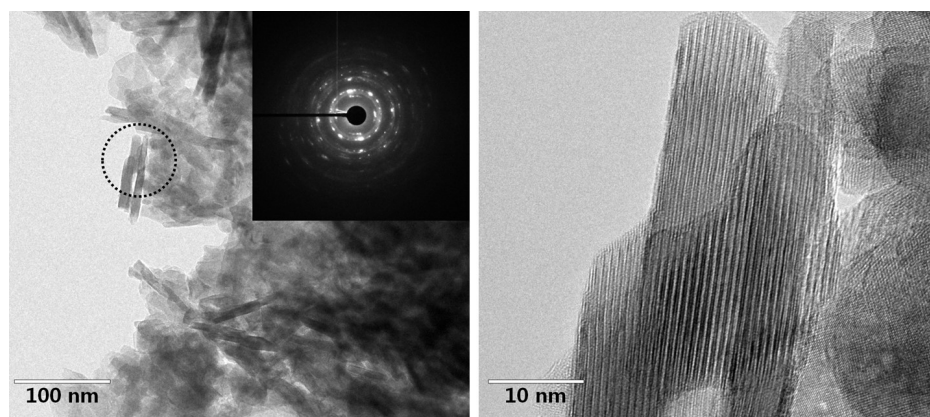


Fig. 5. TEM photographs and SAD of calcined powder at 400°C, prepared with high molecular weight PVA (MW : 153,000)

agglomerates, the particles revealed a relatively uniform spherical shape with a nanometer-size. Interestingly, the nano wire was completely gone at 800°C, the temperature of no existence carbon. This means that the nano wires were developed to crystallized yttria as the oxygen atmosphere is provided after removal of residual carbon.

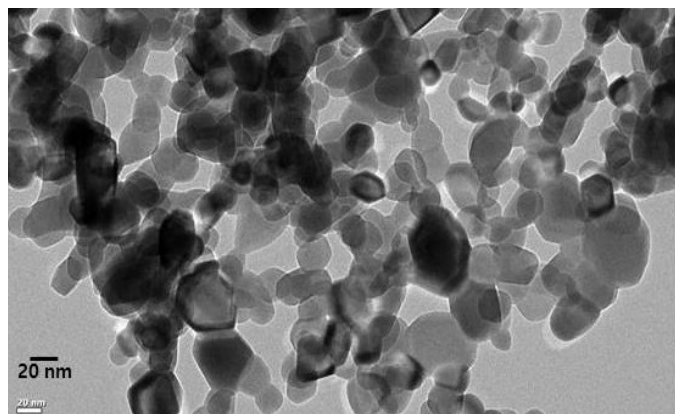


Fig. 6. TEM photograph of fully crystallized yttria powder at 800°C, prepared with high molecular weight PVA (MW : 153,000)

The specific surface areas of the yttria powders calcined at 400°C, 600°C and 800°C with the different-type PVA polymer are presented in Table 1. The BET measurement of the calcined powder at 400°C had the highest specific surface area of 46.0 m²/g in the use of low MW PVA. The powder prepared with high MW PVA showed 39.5 m²/g. These results seem to well match with the powder morphologies as shown in (Figs. 3-5). The larger size of nano wire in the powder prepared with high MW PVA showed lower surface area. In the case of the 600°C, the measured specific surface areas were 29.6 m²/g and 29.4 m²/g, respectively. However, the yttria powder prepared with high MW PVA showed higher surface area of 18.8 m²/g than the case of low MW PVA at the temperature of 800°C. The higher surface area is attributed to the more porous powder structure due to the removal of high MW PVA. Actually, the larger volume expansion during the drying process of the gel precursor with high MW PVA occurred and it could be also related with the more porous powder structure and the higher specific surface area. The porous and agglomerated yttria powders should be ground to fine powders by a simple ball-milling process. According to a previous study [9], the porous powders synthesized by PVA

TABLE 1

BET specific surface areas of synthesized yttria powders at difference calcination temperature and PVA molecular weight

Calcination Temp. (°C)	PVA molecular weight	
	9,000	153,000
400	46.0 [§]	39.5
600	29.6	29.4
800	13.5	18.8

[§] Specific surface area (m²/g)

polymer solution route were easily ground to nano-sized powders by a ball-milling process. In this study, the agglomeration will be removed or minimized by the simple milling process because the powder structure is enough soft and porous to break apart.

4. Conclusions

The PVA polymer solution method produced yttria powder having characters such as nanometer-sized crystallites, high specific surface area. The synthesized yttria powders prepared with various type of PVA showed nano wire morphology during the synthesized process at the low temperature of 400°C. Uncomplete polymer burn-out at the low temperature resulted in yttrium metal phase with carbon compound showing the nano wire single crystals. The nano wire crystal size was increased as the molecular weight of PVA increase. The synthesized yttria powders calcined at 800°C showed spherical shape with an average particle size of 30 nm having a surface area of 18.8 m²/g. The exothermic reaction during the oxidation of organic polymer in the calcination process contributed to the porous microstructure of fully crystallized yttria powder. Finally, the PVA type had an influence on the synthesis behavior and powder morphology on the pre- and after polymer burn out process.

REFERENCES

- [1] F.M.B. Marques, G.P. Wirtz, *J. Am. Ceram. Soc.* **74**, 598 (1991).
- [2] C. Brecher, G.C. Wei, W.H. Rhodes, *J. Am. Ceram. Soc.* **73**, 1473 (1990).
- [3] A.L. Micheli, D.F. Dungan, J.V. Martese, *J. Am. Ceram. Soc.* **75**, 709 (1992).
- [4] Y. Tsukuda, *Jpn. Ceram. Soc. Bull.* **23**, 456 (1988).
- [5] R. Mangalaraja, J. Mouzon, P. Hedström, *Powder Technology* **191**, 309 (2009).
- [6] T. Ikegami, J. Li, T. Mori, *J. Am. Ceram. Soc.* **85**, 1725 (2002).
- [7] C.H. Jung, H.G. Lee, C.J. Kim, S.B. Bhaduri, *J. Nanoparticle Res.* **5**, 383 (2003).
- [8] C.H. Jung, H.G. Lee, G.W. Hong, *J. Mater. Syn. and Proc.* **9**, 19 (2001).
- [9] S.J. Lee, W.M. Kriven, *J. Am. Ceram. Soc.* **81**, 2605 (1998).
- [10] Z. Huang, X. Sun, Z. Xiu, S. Chen, C. Tsai, *Mater. Lett.* **58**, 2137 (2004).
- [11] S. Subramanian, P. Shanker, H. Venkataraman, *Mater. Lett.* **48**, 342 (2001).
- [12] M.A. Gülgün, M.H. Nguyen, W.M. Kriven, *J. Am. Ceram. Soc.* **82**, 556 (1999).
- [13] M.H. Nguyen, S.J. Lee, W.M. Kriven, *J. Mater. Res.* **14**, 3417 (1999).
- [14] S.J. Lee, E.A. Benson, W.M. Kriven, *J. Am. Ceram. Soc.* **82**, 2049 (1999).
- [15] S.J. Lee, M.D. Biegalski, W.M. Kriven, *J. Mater. Res.* **14**, 3001 (1999).
- [16] S.J. Lee, C.H. Jung, *J. Nanosci. Nanotechnol.* **12**, 800 (2012).