Fabrication of Nano-sized Titanate Powders by an Ethylene Glycol Solution Route

S. J. Lee[1,a], M. J. Lee[2,b], and Y. S. Yoon[3]

[1]Dept. of Advanced Materials Science & Engineering, Mokpo National University, Muan, 534-729, KOREA
[2]Project Evaluation Division, Defense Agency for Technology and Quality Assurance, Seoul, 130-650, KOREA
[3]Dept. of Advanced Technology Fusion, Konkuk University, Seoul, 143-701, KOREA
[a]lee@mokpo.ac.kr, [b]manjonglee@data.re.kr, [c]ysyoon@konkuk.ac.kr

Abstract

Several titanate powders (Al_2TiO_5, $SrTiO_3$, etc.) were synthesized by an ethylene glycol solution route. Titanium isopropoxide and nitrate salts were dissolved in stoichiometric proportions in liquid-type ethylene glycol without any precipitation. The parent precursor sols were dried to porous gels, and then the gels were calcined and crystallized. All synthesized titanate powders had stable crystallization behavior at low temperature and high specific surface area after a simple ball-milling process. A three-component PZT ($Pb(Zr_{0.52}\cdot Ti_{0.48})O_3$) powder was also synthesized successfully by the ethylene glycol method. In this study, the characteristics of the multi-component titanate powders by the ethylene glycol method are examined.

Keywords : Titanate powder, Ethylene glycol, Synthesis, Precursor, Ball-milling

1. Introduction

Recently, a solution-polymerization technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG (ethylene glycol) as a polymer carrier has been developed to establish an easier and high productive form of soft solution processing. The method used in this study is based on the polymerization using ethylene glycol as an organic carrier. The PVA method only works with systems that are water-soluble. However, by using the polymerizing agent, EG, this process can be extended to chemicals that decompose in water, such as titanium isopropoxide. At the optimal amount of EG polymer, the metal ions are dispersed in solution and a homogeneous polymeric network is formed. By the complex polymerizations with ethylene glycol it is possible to synthesize titanate powder using common chemicals, like nitrate-type metal salts and titanium isopropoxide as the titanium source. Titanium isopropoxide is not soluble in water, so other water-soluble chemical routes such as sol-gel methods and PVA methods can not be used. The ethylene glycol method also has a distinct advantage over other sol-gel methods in that it is easier and cheaper.

2. Experimental and Results

Titanium (IV) isopropoxide ($Ti(OC_3H7)_4$) and other cation sources were dissolved in stoichiometric proportions in liquid ethylene glycol. The amount of ethylene glycol was calculated using a ratio of total weight of metal ions from cation sources to the weight of ethylene glycol. Several ratios (1:1~1:10) were tried. In the case of two component titanate powders, nitrates were first added to the ethylene glycol and heated to 60 °C, while mixing, until it was fully dissolved. Then, the titanium (IV) isopropoxide was slowly added, while stirring. The solutions were then allowed to gel for 48 hrs in a drying oven at 80 °C. The dried gels were then heated at various temperatures. The heated, crystallized powders were ball-milled with zirconia media for 12 hrs. Isopropyl alcohol was used as a solvent for the wet-milling.

The yellow-colored, dried precursor gels from the transparent solution were ground by pestle and mortar. In the thermal analysis with the precursors, two exothermic peaks at about 300 °C and 550 °C were observed in all cases. In the ethylene glycol method, the first exothermic peaks at 300 °C was due to the pyrolysis of ethylene glycol resulting in the breaking of the bonds, removal of free organics from metal-ion sources and release of N_xO_y gases. Another exothermic peak at 550 °C was due to the burn out of residual carbon by oxidation. The summary of the one, two and three component titanate powders are listed in Table 1.

TABLE 1. Chemical sources and EG contents in the synthesis of titanate powders

Compound	Crys. temp. [°C]	Spec. surf. area[#] [m^2/g]	Aver. Particle size [μm]
TiO_2	800	9.34 (29.6)	(0.08)
$SrTiO_3$	900	11.21 (13.9)	(2.6)
Al_2TiO_5	800	14.29 (22.0)	(0.33)
Dy_2TiO_5	800	6.78 (17.9)	(0.4)
$CaTiO_3$	700	5.34 (24.5)	(0.41)
PZT[*]	800	5.21 (18.4)	(0.43)

( ):ball-milled powders for 12 h with zirconia media
[*] $Pb(Zr_{0.52}\cdot Ti_{0.48})O_3$ [#] fully crystallized powders

Fig. 1 shows the powder morphology of the ball-milled TiO_2 powders. In the TEM micrograph, fine particles of about 100-40 nm in size were observed. And the BET specific surface area of the ball-milled powder was 29.6 m^2/g. The synthesized TiO_2 powder by the EG method can be an excellent powder for applications of titania in the electronic field in such characteristics of high purity, ultra-fine, and easy control of phase.

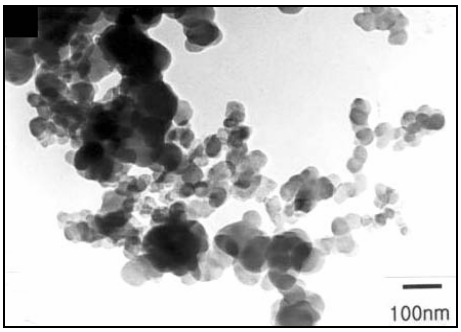

Fig. 1. TEM micrograph of ball-milled TiO_2 powder

In two component titanate powders, most of the powders were quite soft and porous. The amorphous type, as calcined powders, such as aluminum titanate and calcium titanate, showed high specific surface area of 51.96 m^2/g and 25.68 m^2/g, respectively. After crystallization, the specific surface areas abruptly decreased to 14.29 m^2/g and 5.34 m^2/g as shown in Table 1. It means that the as calcined powders are ultra-fine and reactive, so pre-sintering occurred during the crystallization temperature. The ball-milled aluminum titanate and calcium titanate powders showed almost two times or four times larger specific surface areas with sub-micron particle sizes. In the dysprosium titanate, a similar pre-sintering behavior was observed. The SEM micrograph of the porous and crystallized dysprosium titanate powder and the particle size distribution of the ball-milled powder are shown in Fig. 2.

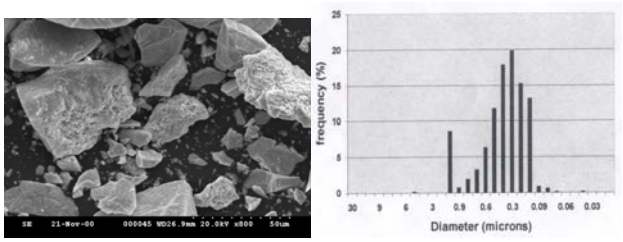

Fig. 2. SEM micrograph of dysprosium titanate powder crystallized at 800 °C and the particle size distribution of the ball-milled powder

In three component titanate powder (PZT), the calcined powder was covered by a crucible and sealed by powder packing during heating process to prevent loss of lead component by evaporation. In XRD observation, PZT was detected at 600 °C, and highest intensity of PZT was observed at 800 °C with a composition of $Pb(Zr_{0.52}\cdot Ti_{0.48})O_3$. However, the XRD intensity gradually decreased above 800 °C. This may be due to a non-stoichiometric composition caused by evaporation loss of the lead component at higher temperatures.

3. Summary

One, two and three component titanate powders were synthesized by the ethylene glycol method. The simple, processable precursors to titanates could be synthesized on steric entrapment of cations by ethylene glycol polymer to avoid selective precipitation and produces homogeneous mixing on a molecular scale. All synthesized titanate powders had stable crystallization behavior at low temperatures and showed high specific surface areas after the ball milling process. The titanate powders synthesized by the EG method will be used widely in various fields of ceramic applications because of its merits, such as cheap and easy processing, high yield, and control of powder properties.

4. References

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