용액연소합성법으로 제조된 ZrO$_2$ 및 3-YSZ 나노입자의 소결거동

김윤성[*], 임준혁[1], 신용섭[2], 김원배[3], Amit U. Limaye[4], Joseph J. Helble[4]

요업(세라믹)기술원, [1]부경대 화학공학과, [2]경성대 환경공학과, [3]인성파우더테크(주),

[4]University of Connecticut

(yunsung_001@yahoo.co.kr[*])

Sintering Behavior of ZrO$_2$ and 3-YSZ Nanoparticles Produced by Solution-Based Flame Synthesis

Y.S.Kim[*], J.H. Lim[1], Y.S. Shin[2], W.B. Kim[3], Amit U. Limaye[4], Joseph J. Helble[4]

KICET, [1]Pukyong National University, [2]Kyungsung University, [3]Insung Powder Tech,

[4]University of Connecticut

(yunsung_001@yahoo.co.kr[*])

Introduction

Zirconia and its derivative, stabilized by the incorporation of stabilizing oxides, such as yttria, are useful in many advanced structural, high-temperature and electrical ceramic applications. The stabilized zirconias generally have low thermal conductivity, high mechanical strength, high fracture toughness, and relatively high thermal expansion coefficients relative to the unstabilized material. Powder characteristics such as particle size and size distribution, however, affect the processing of the ceramic powder and thus affect the utilization of the powder in each of these applications. It has been suggested that ceramic powder consisting of very fine spherical particles and narrow particle size distribution can be used to provide low sintering temperatures, high packing densities, and uniform microstructure in the final product.

Nanoparticles in particular can enhance densification at lower temperatures and produce products with smaller residual pores and finer grain size. For certain applications of ceramic particles, it is useful to have particles of consistent spherical morphology. The control of the shape and the size is thus an important problem in the synthesis of ceramic particles. Nanoparticles can be readily produced by vapor phase routes, but the resulting particles are often agglomerated partially sintered fractal-like structure. Such structures are formed when sintering or coalescence times become long relative to system residence times. Preventing or controlling the formation of these structures therefore requires an understanding of the rate of ceramic nanoparticle sintering in such systems.

The control of both particle synthetic method and subsequent sintering to achieve high density and ultrafine grained microstructure in the sintered bodies is still one of the major challenges in the processing of ceramic materials. The use of crystalline nanoparticles could be the key of achieving

muck lower sintering temperature, better microstructure, improved mechanical and electrical properties and, as a consequence, higher reliability. I it is difficult to use a single simplified model for bulk powder to describe the mixed mechanism of the sintering process of the nanoparticles. To understand on sintering behavior of the nanoparticles, possible mixed mass transport mechanism, which can match with the previous studied sintering model, is firstly proposed, and then the related kinetic equation of the grain growth can be derived, as can proceed on sintering study for bulk powder. It was thought that diffusion process between nanoparticles ranged from dozens to several hundred nanometers in even aerosol system could be explained by various mass transport mechanisms based on the classical sintering model.

In this study, sintering rates were measured during the initial stage of high temperature (1073 to 1273K) sintering for spherical crystalline ZrO_2 and 3-YSZ (3mol% yttria stabilized zirconia) nanoparticles produced by solution-based flame synthesis. And mixed diffusion mechanisms of solid state sintering process were applied to provide a comprehensive acting mechanism of the initial stage in sintering process of the nanoparticles. Rates were compared with literature data to determine whether the presence of the stabilizing agent affected the sintering rates under these conditions, and to determine the dominant mechanisms of sintering for nanoparticles under these conditions when the particle are present in an aerosol stream.

Experimental

Nanoparticles of ZrO_2 and 3-YSZ ranging in size from 20 to 100nm were produced by a solution-based flame synthesis method. A schematic diagram of the system used to generate these nanoparticles is shown in Figure 1. Nanoparticles were produced by atomizing a combustible spray containing the ceramic precursor, zirconium nitrate, and passing this spray into the core region of a methane-oxygen-nitrogen flat flame. At the exit of the particle production reactor, the gas stream containing the nanoparticles is extracted with a gas quenched sampling probe. The Sample stream is then passed through an eleven stage low pressure impactor (LPI) tom remove all particles with an aerodynamic diameter greater than 100nm. The gas stream, now containing only nanoparticles smaller than 100nm, is then passed to an aging chamber to provide sufficient residence time for particle coagulation.

At the conclusion of the coagulation step in the aging chamber, particles were passed to the sintering section of the apparatus (Figure 1). This section of the system consists of a 66cm long, 2.1cm diameter quartz tube contained within a resistance heated tube furnace. Furnace temperatures in the sintering zone were held at constant at 1073K, 1173K, or 1273K as measured by a Type K thermocouple. Nanoparticles ranging from 20nm to 100nm were introduced into the sintering furnace in air flow rate of 0.2l/min. The residence time for the nanoparticle in the heating furnace was calculated 19.05s at 1073K, 17.42s at 1173K, 16.05s at 1273K, respectively.

To analyze the particles, an electrostatic precipitator (ESP) was first used to separate the

nanoparticles from the gas stream by deposition onto a transmission electron microscope (TEM) (Model 420, Phillips) grid. TEM images were then examined to provide an indication of particle size, neck size, and dihedral angle in a sintered pair. Only sintered particle pairs demonstrating a size difference of less than 10% between the two primary particles were considered. At least 60 TEM pictures were used to investigate neck growth rate at any given temperature. A TSI model 3934 scanning mobility particle sizer (SMPS) was also used to obtain on-line measurement of the particle size distribution in the range of 18-900nm.

Results and Discussion

Fig. 2(a) shows the effect of sintering temperature on neck growth rate of ZrO_2 nanoparticles. The higher sintering temperature, the higher neck growth due to vigorous mass transport through surface curvature. At given sintering temperature, the neck size could be greater with decreasing particle size. With increasing sintering temperature, sintering mechanism changed from the total surface transport mechanism to surface diffusion. This results from vigorous mass transport path through particle surface in the higher heating condition at highest temperature. The calculated neck growth rate could be overestimated neck size with lower particle size under 70nm. Activation energy of surface diffusion for the ZrO_2 nanoparticles was calculated to 240kJ/mol. This value is a little lower than that predicted by Kanters et al. When the particle size was smaller than 70nm, the calculated size was higher than that those obtained from the experiment.

Effect of sintering temperature on neck growth rate of 3-YSZ nanoparticles is shown in Fig. 2(b). Experimental result was not agreement with calculated curves using two Q_{SD}'s even in higher particle size. For ceramic sintering, the number of free surface around spherical particle is able to vastly increase with the decrease in particle size, but local atomic environment in which Zr^{+4} ions are moving could be retarded by added yttria ions. Therefore, activation energy for 3-YSZ is much more than that for the unstabilized zirconia. Activation energy for surface diffusion of the particles might be feasible to consider by 478kJ/mol.

Conclusion

The effects of initial particle size and sintering temperature on the neck size of ZrO_2 and 3-YSZ nanoparticles were investigated. Neck growth rate overestimated with decreasing the particle size. With increasing sintering temperature, dominant sintering mechanism of ZrO_2 nanoparticles changed from total surface transport to surface diffusion due to vigorous mass transport between the two particles. For 3-YSZ nanoparticles, neck growth rate was lower than the counterpart. It was thought that mass transport between crystals in ZrO_2 nanoparticles could be confined by added yttria during the initial stage of sintering. Activation energy of surface diffusion of ZrO_2 and 3-YSZ nanoparticles was calculated to 240kJ/mol and 478kJ/mol, respectively.
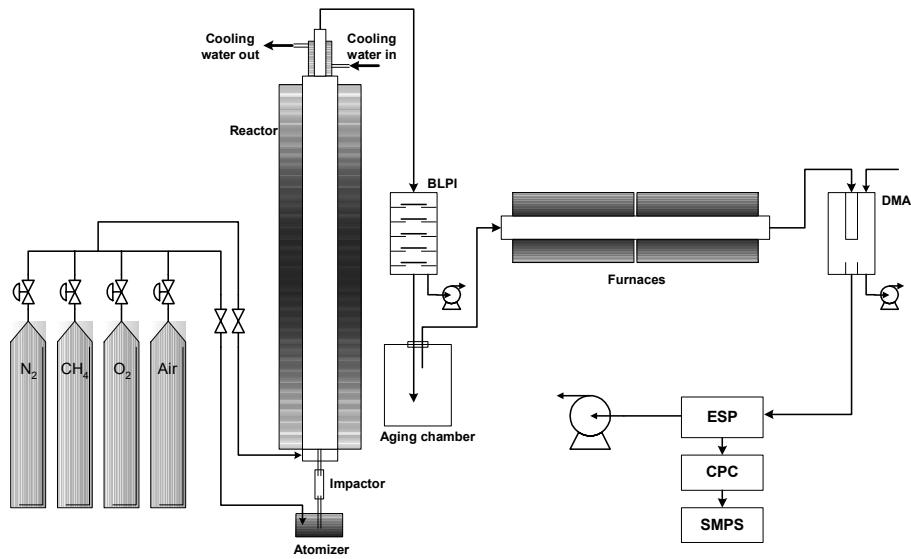
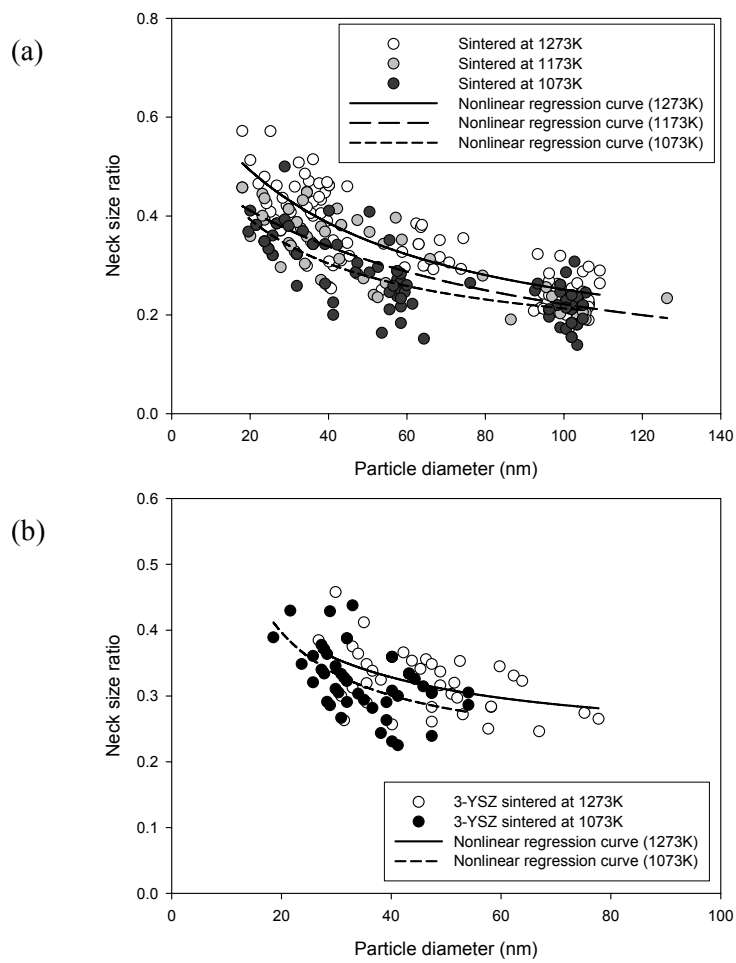Fig.1. Schematic diagram of experimental apparatus for nanoparticle synthesis and sintering.

Fig.2. Effect of sintering temperature on the neck growth rate of (a) ZrO_2 and (b) 3-YSZ
nanoparticles produced by solution-based flame synthesis.