EFFECT OF ANNEALING ON THE MECHANICAL PROPERTIES OF POROUS TITANIA NANOPARTICLE AGGLOMERATE FILMS

O. A. Ogunsola and S. H. Ehrman, Department of Chemical Engineering
University of Maryland, College Park, MD 20742

I. INTRODUCTION

Nanoparticles are used as starting materials for porous materials. Porous films made from titania nanoparticle agglomerates have a variety of applications such as photocatalysts in wastewater treatment [Yu et al., 2003], hydrophobicity in window self-cleaning [CMN, 2002] and electrodes for low cost solar cells [Grätzel et al., 1997]. Titania nanoparticulate films have been successfully made via a hybrid process based upon gas-to-particle conversion and particle precipitated chemical vapor deposition. At the stage of collection, no further chemical reaction occurs. The process offers the advantages of single-stage, atmospheric, solvent-free, and low substrate temperature operation, enabling deposition onto materials for which thermal degradation is a limiting factor [Nguyen et al., 2002]. Generally, agglomerated nanoparticles are formed when the sintering rate between primary particles is faster than the collision rate. For the production of porous films, agglomerated particles are advantageous as they lead to a highly porous microstructure. Generally, strong chemical bonds are found between primary particles (because they are partially sintered at high temperatures) and weak van der Waals bonds exist between small agglomerates that collide together at low temperatures [Friedlander, 2000]. The final microstructure of the film that we have made is highly porous (98%) but of low mechanical strength due to the presence of the weak van der Waals bonds. Annealing the films increases the interconnectivity of the particles by enhancing old chemical bonds and forming new chemical bonds in replacement of the van der Waals bonds. This will increase the mechanical strength of the film and ensure that it does not collapse in its end use, causing reduction in porosity, which reduces its productivity. The increase in interconnectivity is accompanied by a change in the primary particle and agglomerate sizes. The objective of the work described here is to gain a better understanding of how annealing affects the mechanical properties of these porous titania nanoparticle agglomerate films. This will enable engineering of the films to be stronger without loss of their valuable porosity.

II. EXPERIMENTAL

The preweighed silicon substrate is placed on top of the cooling stage. The furnace is preheated for four hours to obtain the desired furnace processing temperature. In these experiments, the three zones of the furnace were set at 1000 °C. The cooling stage water temperature was maintained at 15 °C. The bubbler was heated to 50 °C to increase the vapor pressure of the titanium tetra isopropoxide (TTIP). The feed lines going into the reactor chamber were heated to 150 °C to prevent condensation of the TTIP vapor. Oxygen was allowed to flow in at 900 sccm (standard cubic centimeters per minute). Argon, the carrier gas, was fed into the gas-drying unit at 325 sccm. The TTIP vapor is bubbled out at 0.000008 moles/min by opening the exit and entrance valves of the bubbler. The film on the silicon substrate and powder were annealed in air at 400 to 1000 °C for 12 hours each.

III. RESULTS AND DISCUSSION

Characterization of the powder has been conducted using a variety of characterization methods. The Transmission Electron Microscope (TEM; Hitachi 600AB) was used to determine the structure of the agglomerated particles and size distribution of primary particles. The Scanning Electron Microscope (SEM; JEOL SEM 5400) was used in film thickness measurements. The Brunauer-Emmett-Teller gas adsorption method (BET; Quantachrome Nova 1200) was used to perform surface area measurements from which size of the particles was estimated. TEM results, in Figure 1, show a slight increase in particle diameter when the titania film was annealed at 400 and 600 °C. There is a big increase when annealed at 800 °C and a bigger increase at 1000 °C. The type of change seen in the primary particle size is also reflected in the percentage porosity change in the film. The only marked difference is that there is a higher jump in porosity change when annealed at 1000 °C. BET surface area measurements ranges from 40 m^2/g of the unannealed film to 4.3 m^2/g when annealed at 1000 °C. The BET results show a loss of microporosity in the film when annealed.

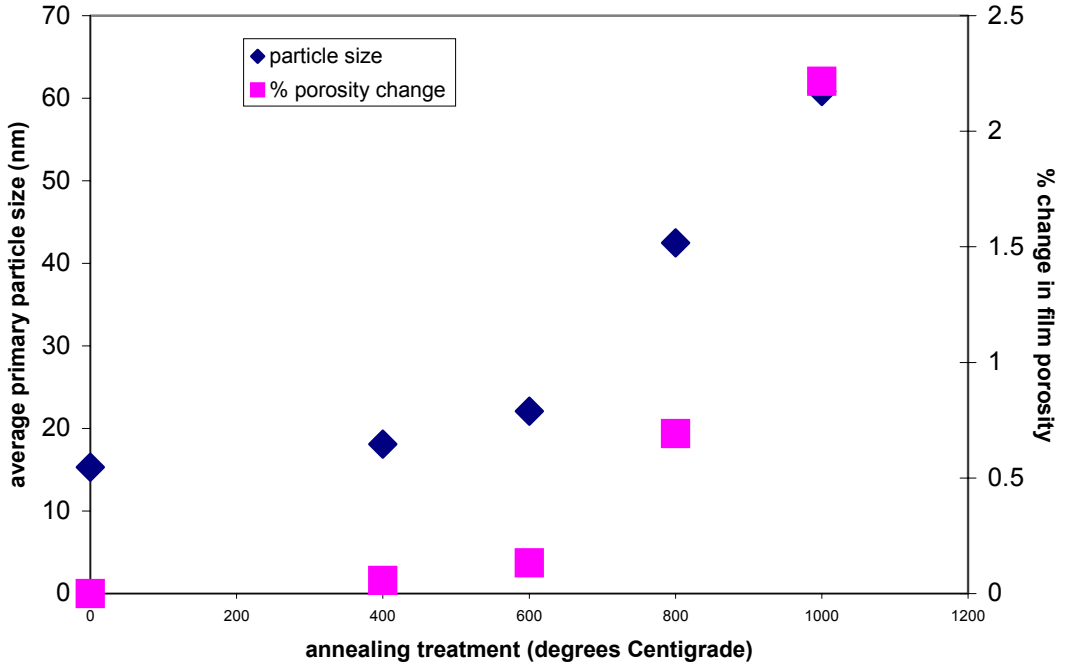

Figure 1. TEM and porosity results.

The elastic modulus of the films was predicted using the Gaussian Random Field (GRF) method [Roberts and Garboczi, 2002]. The GRF is a good method to predict the upper bound of the elastic modulus of porous solids. Evidence is seen in the comparable GRF theoretical prediction and the experimental nanoidentation results of an untreated alumina film (made via the same process). The difference seen is because the model assumes all the bonds in the film are chemical bonds. The film however has a mix of chemical and van der Waals bonds. The overall porosity in the film is still very high (96%), even when annealed at 1000 °C. However, the slight changes in the film porosity give rise to changes in the elastic modulus. Figure 2 shows how there is no major change in elastic modulus when annealed, except at 800 and 1000 °C. The rate of change in particle size does not correspond to the rate

of change in elastic modulus. This suggests that particle size does not have a total 100% effect on the strength of the films. One possible interpretation could be that, a combination of the particle size and the agglomerate size is what affects the elastic modulus.

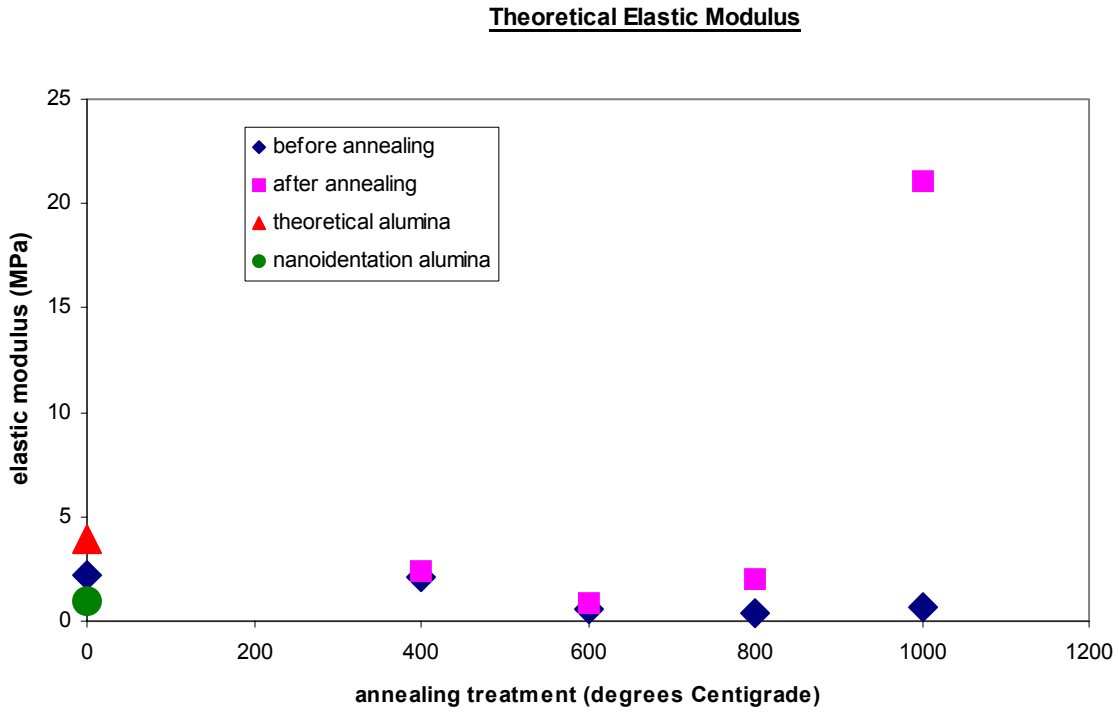

Figure 2. Elastic modulus prediction.

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